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Interfacial Coupling between Immiscible Polymers: Reactive Interface between Polysulfone and Amorphous Polyamide

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ABSTRACT: The coupling reaction at the immiscible polymer−polymer interface formed between bilayer films composed of amorphous polyamide (aPA) and polysulfone (PSU) incorporating different functional groups was monitored by X-ray photoelectron spectroscopy (XPS). The overall coupling reaction was consistent with pseudo-first-order kinetics, and the process was controlled by the reaction between functional groups situated at the interface. Anhydride groups attached to PSU, both phthalic anhydride and maleic anhydride, showed significantly faster and higher reactivities than epoxide and triazine groups in the reaction with the primary amine end group of aPA. The saturation areal density of the copolymers at the interface, Σ^*, changed depending on the architecture of the resultant copolymers, which suggested that Σ^* would be determined by the interfacial area occupied by a single copolymer chain at saturation.

Introduction

In reactive processing, where two immiscible reactive polymer melts are mixed, it is understood that because of the immiscibility of the two component polymers the only opportunity for encounter between the functional groups is within the interfacial region, which is typically only a few nanometers thick. Furthermore, practical considerations require that the reaction time falls in the range 30 s to 5 min.[1−4] Thus, to determine the optimum processing conditions, it is essential to carry out careful investigations of the reaction kinetics. Yet, despite the importance of quantitative studies of the coupling kinetics, there are only a limited number of experimental results available in this area. These fall under two categories: investigations carried out in the presence[5−9] or absence of shear.[10−14] We believe that there are several important points to consider in order to correctly determine the intrinsic reaction kinetics in the melt state between two functional groups attached to immiscible polymer pairs.

First, for reactions under shear conditions, it is necessary to take into account the contribution of the increased interfacial area on the reactivity, as the particle size is reduced. It is widely known that the particle size is controlled not only by the interfacial tension changed by the degree of copolymer formation at the interface but also by the melt viscosity of the component polymers and the shear rate.

Second, in some systems it is also necessary to consider the contribution of micelle formation between the resultant copolymers. For example, in reactive melt mixing between polystyrene end-functionalized with primary amine groups (PS−NH_2) and polyisoprene (PI) end-functionalized with anhydrides, it is reported that an ordinary sea-island morphology was formed by a slower, less-reactive pair with aromatic amine incorporated to PS, whereas molecular scale self-assembly into cylindrical micelles was generated by a faster, more reactive pair with aliphatic amine incorporated into PS.[5] In micelle-forming systems such as in the latter example, the removal of copolymers from the interface would give rise to a significant increase in the overall reactivity, induced by the external force.

A recent study found that it is necessary to consider the molecular architecture itself of the copolymers formed in situ, as this can lead to the stabilization or destabilization of the copolymers at the interface.[15,16] For example, we have found, using the same reactive pair (anhydride and primary amine) and immiscible polymer pairs (polysulfone and polyamide 6) with the same molecular weights, that in situ formed block copolymers with a linear structure were easily removed from the interface, as indicated by micelle formation in the matrix. On the other hand, graft copolymers with trunk chains located in the dispersed phase remained in stable form at the interface, whereas graft copolymers with trunk chains situated in the matrix were again removed from the interface in the form of micelles. Thus, the diversity of copolymers formed at the interface can complicate determination of their reactivity in heterogeneous coupling. It is also important to emphasize here that micelle formation can take place even in a symmetric copolymer forming system under dynamic condition, whereas a copolymer with $0.3 < f = N_A/(N_A + N_B) < 0.7$ was predicted to be thermodynamically stable at the interface under quiescent condition.[17] In the formula above N_A and N_B are the degrees of polymerization of the A and B blocks, respectively.

Third, care should be taken in the extrapolation of kinetic results on dilute model compounds to condensed polymer systems. For example, some researchers have attempted to predict the true intrinsic kinetics between

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two reactive polymers from the reaction between low molecular weight (LMW) model compounds, LMW/LMW, in solution[18,19] or using a LMW/polymer system.[18−20] However, Ferrari and Baker have expressed alarm at this method, because it does not take into account a kinetic excluded volume effect caused by the functional groups shielded by polymer chains in the melt.[19]

Recently the groups of Fredrickson[21,22] and O'Shaughnessy[23−26] independently developed theoretical predictions of the kinetics of the coupling reaction taking place at immiscible polymer−polymer interfaces under quiescent conditions. Fredrickson's group assumed that the overall process was controlled by diffusion of the reactive chains and found that there would be three time regimes during the reaction resulting in a change of the areal density of the copolymers formed at the interface, Σ.[22] A linear growth of Σ in time, t, in the initial time regime, a $t^{1/2}$ growth in the intermediate time regime, and a $(\ln t)^{1/2}$ growth in the late time regime were predicted. Müller verified the $t^{1/2}$ dependence of the intermediate regime by Monte Carlo simulations (MCS).[27] However, he did not observe the linear dependence of the initial time regime. Instead he found that the initial reaction rate was higher by about an order of magnitude than predicted by the theory and decayed with time.

O'Shaughnessy and co-workers categorized kinetics according to the reactivity between reactive pairs and on reaction stages. They predicted that in the initial stage the reaction kinetics would be controlled by reaction between reactive pairs with the linear growth of Σ in t following the mean field theory but that in later stages it would be controlled by diffusion of reactive chains. Three distinct kinetic sequences were proposed, which gave rise to different types of reaction kinetics as a function of time, such as $\Sigma \sim t/(\ln t)$, $\sim t^{1/2}$, $\sim t^{1/4}$, and $\sim t^{1/8}$.[25, 26]

In contrast, in our most recent work the coupling at the immiscible polymer interface was viewed from a completely different aspect, in which the reaction was considered to occur from the formation of a two-dimensional monolayer at the interface plane by copolymers formed in situ.[28] It was clearly shown that the overall kinetics followed an apparent first-order behavior in the quantity $(\Sigma^* - \Sigma)$, where Σ^* was the saturation areal density of copolymers at the interface. Furthermore, it was found that the rate-determining step involved a process of filling vacant sites available on the interface and that the predicted model with $\Sigma \sim -\exp(-t)$ fit the data in the whole time regime quite well. Surprisingly, it was also demonstrated that the model was widely applicable to other coupling reactions held at polymer−polymer interfaces, even to reactions involving multifunctional reactive chains, leading to cross-linking at the interface. In the past, the reaction kinetics at interfaces have always been analyzed using the reactant concentration in bulk in the literature. Therefore, the approach here is unique, which utilizes the parameter $(\Sigma^* - \Sigma)$ defined as the residual amount necessary to reach the saturation areal density of copolymers at the interface. This is an experimentally measurable quantity, which represents the amount of free area at the interface.

The focus in the present paper is the study of the coupling kinetics at quiescent conditions in bilayer films composed of amorphous polyamide (aPA) and different reactive polysulfones (PSU). The amount of the functional groups incorporated in the PSU chain was limited to 38%, by combining reactive and nonreactive PSU as necessary. Transmission electron microscopy (TEM) measurements were used to verify that there were no micelles formed in the vicinity of the interface. Finally, the physical meaning of the Σ^* parameter proposed in our model is clarified.

Table 1. Sample Characteristics

sample	M_n	M_w	T_g (°C)	functionality[a] μmol/g	functionality[a] no./chain
nf-PSU	6050	20 120	170	0	0
PSU-*ω*-PAH	7000	19 700	164	143	1.00
PSU-*g*-MAH	7540	19 270	165	139	1.05
PSU-*ω*-EP	6970	20 010	172	55	0.38
PSU-*ω*-TRI	6200	19 740	172	102	0.63
aPA	8400	32 800	97	119	1

[a] The functionality of PAH, MAH, EP, and TRI incorporated to PSU was determined by infrared spectroscopy, potentiometric titration, ^{1}H NMR spectroscopy, and elemental analysis of nitrogen, respectively.

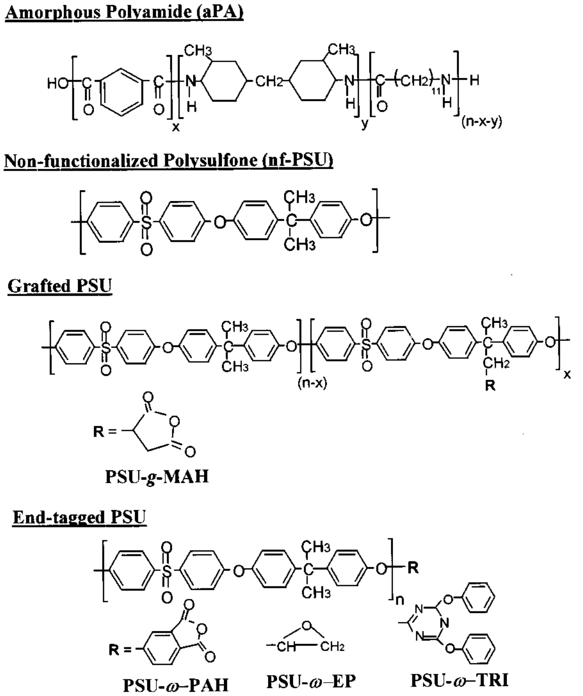

Figure 1. Chemical structures of aPA and PSU samples. (Values of x and y in aPA are not well-defined.)

In this paper, the kinetic order observed in experiments is given the label "pseudo-". This is to account for cases where second-order kinetics become "pseudo-first-order", when one of the concentration terms is constant. In other papers, the kinetic order is simply given by the sum of exponents in the concentration terms of the kinetics equation.

Experimental Section

Materials. Polymer specimens used in this study and their characteristics are listed in Table 1 and depicted in Figure 1. In addition to nonfunctionalized PSU (nf-PSU), four different types of PSUs functionalized with phthalic anhydride (PAH), maleic anhydride (MAH), epoxide (EP), and triazine (TRI), either at the middle of the chain (*g*) or at the end of the chain (*ω*) were prepared by following the synthetic procedures given in the literature.[29−32] Amorphous polyamide (aPA) containing one terminal primary amine group per chain was obtained from EMS Japan. The concentration of functionality in the PSUs was adjusted to 55 μmol/g, by mixing the reactive PSU

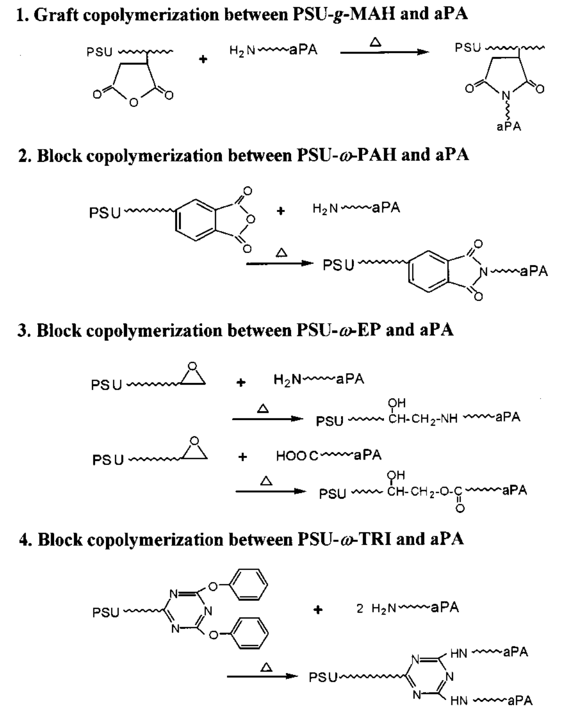

Figure 2. Schemes of the interfacial reaction.

and nf-PSU. Two component polymers with similar molecular weights were used in this study.

Bilayer films consisting of an aPA layer of ca. 0.5 mm thickness and a PSU layer with 200−500 nm thickness were prepared using the method described previously.[33] The aPA substrate was prepared by hot press melting the sample at 200 °C between silicon wafers. The PSU film was obtained by spin-casting from a chlorobenzene solution onto a silicon wafer, which was then mounted on the aPA substrate by the floating-on-water and pickup technique. The bilayer film was dried under vacuum at 50 °C for 24 h. In the kinetic study, the bilayer film was heated in an annealing box at 200 °C for a given time. Then, the PSU layer was throughly removed by chlorobenzene, and the exposed interface on the aPA side was analyzed by X-ray photoelectron spectroscopy (XPS) to determine the amount of copolymers formed in situ at the interface. Chlorobenzene was chosen because it was a good solvent for PSU and it neither dissolved nor swelled aPA. Details of the calculation will be given later.

Interfacial Analysis. The surface composition of the exposed interface was investigated using a Perkin-Elmer PHI 5500 X-ray photoelectron spectrometer. The spectra were collected using a monochromatized Al Kα source (1486.6 eV) operated at 14 kV and 300 W with a takeoff angle of 45°. The survey scan and the multiplex scan were measured under 187.85 and 23.50 eV of pass energy, respectively. The pressure inside the spectrometer sample chamber was held below 5×10^{-8} Torr during the analyses. The C 1s binding energy of the hydrocarbon component was adjusted to 284.6 eV by a neutralizer and used as a reference. PHI software was used to obtain peak areas, to calculate atomic concentrations and to fit the photopeaks with Gaussian−Lorentzian curves.

Results and Discussion

Interfacial Reactions. Coupling reactions examined in this study are given in Figure 2, in which copolymers with different architectures (Figure 3) are shown to be formed at the interface. Through the reaction with the NH_2 end group of aPA, PSU-*g*-MAH forms a graft copolymer with PSU as trunk chains, whereas PSU-ω-PAH forms a linear block copolymer. On the other hand, the reactions of PSU-ω-TRI and PSU-ω-EP with aPA are rather complicated. In the case of PSU-ω-EP, the epoxide group incorporated at the PSU chain end will react either with the primary amine end group of aPA or with the other carboxylic acid end groups of aPA. If both chain ends of aPA participate in the reaction, a triblock copolymer with a loop structure situated in the aPA phase will be formed; however, if only one end of the aPA chain reacts, a diblock copolymer with a linear structure will be generated. In the analogous reaction between PSU-ω-EP and monodisperse PS end-labeled with NH_2 carried out in chlorobenzene at 60 °C, the GPC chromatogram showed only a peak corresponding to a linear diblock copolymer so that the proportion of triblock could be considered to be very small.[34]

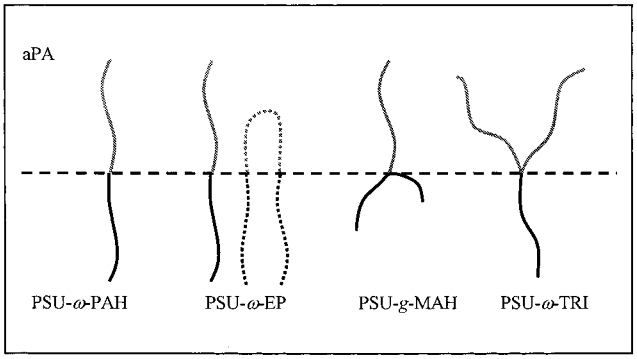

Figure 3. Architectures of resultant copolymers.

Furthermore, the triazine group incorporated into the PSU end results in a y-shaped copolymer originated from two aPA chains and one PSU chain unless there is steric hindrance, as confirmed by GPC analysis in the reaction between monodisperse PS−NH_2 and PSU-ω-TRI.[34] In the literature on reactive blending, reactions involving the triazine group do not appear except for our previous work.[29,34]

XPS Spectra. X-ray photoelectron spectroscopy (XPS) was chosen as a tool for determination of the amount of copolymers generated at the interface. Parts a and b of Figure 4 show survey scans of aPA and nf-PSU, respectively. The spectrum of aPA clearly shows the N 1s photopeak at 400 eV with a trace of inorganic silicon impurity originating from the Si wafer and that of PSU shows two characteristic peaks originating from sulfur, S 2s at 231 eV and S 2p at 168 eV.

Parts a and b of Figure 5 show C 1s and O 1s photopeaks of aPA, respectively, obtained by the multiplex scans. The C 1s photopeak of aPA shown in Figure 5a clearly showed the contribution of the carbonyl group in the amide linkage at 287.8 eV. Both the O 1s photopeak from the carbonyl group at 531.4 eV (Figure 5b) and the N 1s photopeak from the amide linkage and the primary amine end group located at 399.8 eV (Figure 5c) appeared as one broad Gaussian peak.

On the other hand, parts a−c of Figure 6 show C 1s, O 1s, and S 2p photopeaks of nf-PSU, respectively. The C 1s photopeak of nf-PSU shown in Figure 6a did not have any photopeak above 286.3 eV except for a contribution from a shake-up satellite observed at ca. 291 eV. Furthermore, the O 1s photopeak shown in Figure 6b indicated two major peaks, a larger one observed at 531.6 eV assigned to a S=O bond and a smaller one at 533.2 eV assigned to an ether oxygen. In Figure 6c, the S $2p_{1/2}$ and S $2p_{3/2}$ photopeaks were observed at 168.7 and 167.4 eV, respectively. These observed photopeak positions and their assignments are listed in Table 2 with literature values shown in parentheses.[35]

Table 3 summarizes surface compositions for the two component polymers estimated by the multiplex scans, when the contribution of Si is excluded. The obtained values for nf-PSU showed a good agreement with the values calculated from its chemical structure. Therefore, the characteristic photopeak of the N 1s from aPA and that of the S $2p_{3/2}$ from PSU were chosen as probes for the determination of the copolymer amount located at the exposed interface after the unreacted PSU chains were removed by solvent.

Calculation of Areal Density of Copolymers (Σ). Parts a and b of Figure 7, respectively, show changes in the atomic concentration ratio of S/C and N/C at the exposed interface on the aPA side. The results clearly indicate that the ratio of S/C increases with annealing time; however, that of N/C decreases in all systems. As the interfacial reaction proceeded, there was a tendency for the shoulder of the amide C 1s photopeak at 287.8 eV to decrease and for the O 1s photopeak to become asymmetric due to the contribution from the two oxygen states (S=***O***, −***O***−) of PSU, as shown in Figure 8, parts a and b, respectively. Thus, it was confirmed that the increase of the S/C ratio and the decrease of the N/C ratio were due to the covering-up of the polyamide surface by the PSU comonomer of the copolymer formed by the interfacial reaction.

The ratio $(S/C)/(S/C)_{PSU}$ normalized by the S/C value of the neat PSU and the ratio $(N/C)/(N/C)_{aPA}$ normalized by the N/C value of the neat aPA can be expressed by the following equations[36]

$$\frac{(S/C)}{(S/C)_{PSU}} = 1 - \exp\left\{-\frac{Z}{\lambda \sin(90° - \theta)}\right\} \qquad (1)$$

$$\frac{(N/C)}{(N/C)_{aPA}} = \exp\left\{-\frac{Z}{\lambda \sin(90° - \theta)}\right\} \qquad (2)$$

where Z is the thickness (nm) of the PSU comonomer overlayer on the aPA surface, θ is the takeoff angle, and λ is the average attenuation length (nm) of the electrons for C 1s, N 1s, and S 2p. Under the present experimental conditions (energy of Al Kα line = 1486.6 eV, $\theta = 45°$), λ was estimated to be 3.5 nm.[37]

Once the value of Z is obtained, the areal density of the copolymers located at the interface, Σ (chains/nm^2), can be estimated from the following formula[38]

$$\Sigma = N_{av} d Z / M_n \qquad (3)$$

where N_{av} is Avogadro's number and d and M_n are the mass density and the number-average molecular weight of PSU, respectively.

Time Dependence of Σ. Figure 9 shows the Σ values estimated for different reactive pairs using the method mentioned above. In this figure, both Σ values calculated from the S/C ratio (closed marks) and the N/C ratio (open marks) were plotted together. In the PSU-*ω*-TRI/aPA system, the contribution of nitrogen originating from the triazine group underestimates the Σ value so that the Σ value was calculated only from the S/C ratio.

It was demonstrated that the overall reactivity of various PSUs with the primary amine end group of aPA decreased in the order of PSU-*ω*-PAH > PSU-*g*-MAH > PSU-*ω*-EP > PSU-*ω*-TRI on the time scale we studied. The reactivity was very high in both anhydrides, with the copolymer amount reaching constant values in 10−15 min. On the other hand, epoxy and triazine groups reacted slowly and the copolymer quantity did not reach constant values even after 30 min of heating.

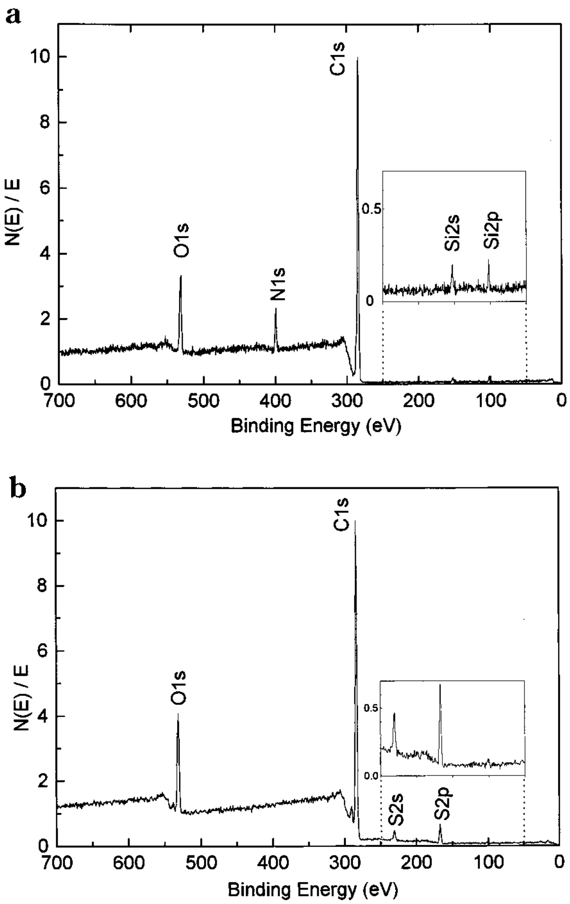

Figure 4. XPS survey spectra of (a) aPA and (b) nf-PSU.

If our results on the time scale of the reaction are compared to other published data, it is notable that some reactions involving similar reactive pairs to ours take a very long time. For example, the reaction held at the interface between monodisperse end-functionalized PS−NH_2 and PMMA−anhydride took as long as 70−100 h,[12] and that held at the interface between PS−NH_2 and styrene−maleic anhydride random copolymer (SMA) took 25−250 h according to estimated values obtained by exponential fitting.[13] Here both systems were analyzed by forward recoil spectroscopy (FRES). On the other hand, the reactions of SMA either with nylon 11 or with butadiene−acrylonitrile copolymer (ATBA) having the NH_2 group located at both chain ends were terminated in 0.5−3 h according to measurements by infrared spectroscopy.[14] Furthermore, the grafting reaction of end-functionalized PS−COOH onto epoxy-rich cross-linked epoxy surface observed by FRES reached completion in ca. 50 min.[11]

The long time scale of the reaction is likely due to the inclusion of the contribution of copolymers located in the bulk in the estimated Σ value, since the time scale was much larger than that estimated assuming that either diffusion of reactive chains to the interface or reaction between functional groups located at the interface would determine kinetics. In our analysis by XPS, the amount of copolymers measured was located solely at the interface so that the termination of the reaction was observed when the interface was filled with copolymers. In the short time systems described,[11,14] the formed copolymers could not leave the interface because

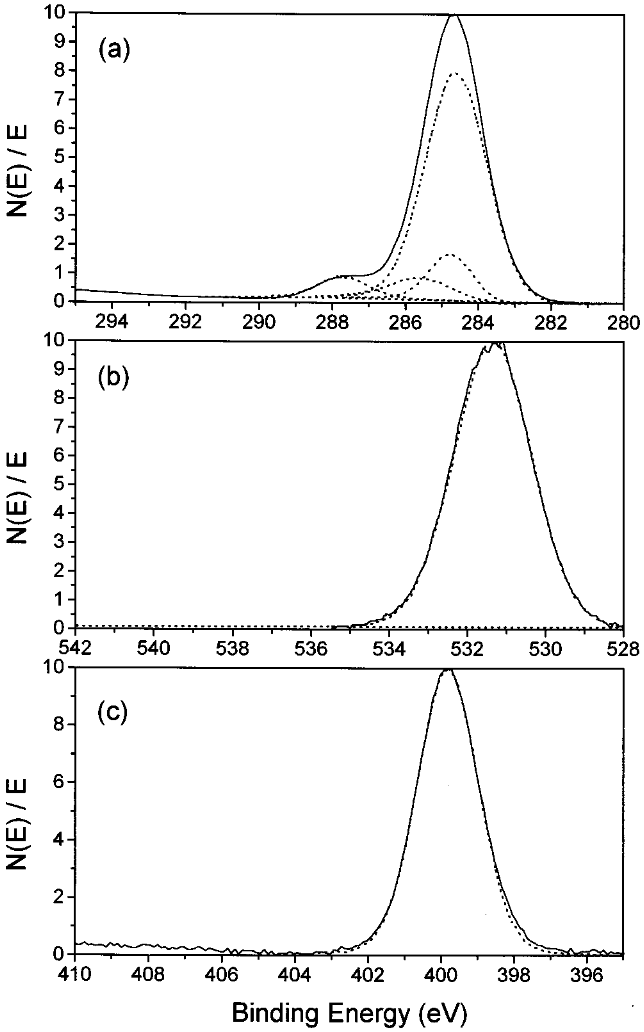

Figure 5. (a) C 1s photopeak, (b) O 1s photopeak, and (c) N 1s photopeak of aPA.

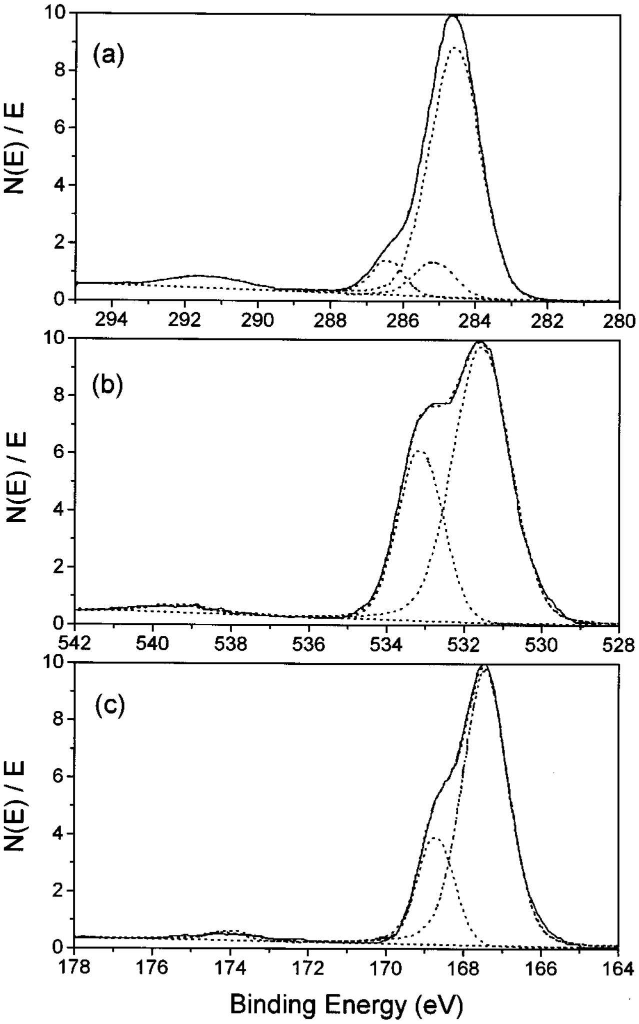

Figure 6. (a) C 1s photopeak, (b) O 1s photopeak, and (c) S 2p photopeaks of nf-PSU.

of cross-linking[14] and grafting onto the solid surface,[11] respectively. So the obtained results are the values for copolymers located only at the interface.

On the other hand, in the analysis by FRES[12,13] the measurement could include both interface and bulk copolymer contribution. The copolymers initially formed at the interface could move on to the bulk, e.g., in the form of microemulsions leading to long reaction times. The departure of the copolymers from the interface could be facilitated by an undulated interface with a lower χN value and the asymmetry in size of copolymers formed at the interface. (Even copolymers formed between so-called monodisperse polymers have the possibility to form asymmetric copolymers because the polydispersity is not exactly 1.0.) In this case, the reaction can continue for a long time, even after the interface is saturated by copolymers. Indeed, formation of microemulsions has been observed in the vicinity of the interface.[13] Under such conditions there would be another candidate for the rate-determining step after the stage of the interface saturation, namely the creation of a new interface by the removal of copolymers. Thus, kinetics with long reaction times are probably controlled by this physical process.

It is interesting to notice here that the positive Σ values were observed even for nf-PSU and for all systems without heating. This is probably caused by some intermolecular interactions between the two component polymers, e.g., hydrogen bonding between the

Table 2. Photopeak Positions and Assignments of aPA and nf-PSU[a]

	aPA		nf-PSU	
C1s	284.6 eV (284.8 eV)	aromatic $\boldsymbol{C}$	284.5 eV (284.7 eV)	aromatic $\boldsymbol{C}$
	284.9 eV (285.0 eV)	$-\boldsymbol{C}\mathrm{H}_2-\boldsymbol{C}\mathrm{H}-$	285.1 eV (285.3 eV)	$\boldsymbol{C}-\mathrm{S}$
	286.0 eV (286.0 eV)	$-\mathrm{CONH}-\boldsymbol{C}\mathrm{H}_2-$	286.3 eV (286.3 eV)	$\boldsymbol{C}-\mathrm{O}-\boldsymbol{C}$
	287.8 eV (288.0 eV)	$-\boldsymbol{C}\mathrm{ONH}-$	291.4 eV (291.5 eV)[b]	shake-up
O1s	531.4 eV (531.4 eV)	$-\mathrm{C}\boldsymbol{O}\mathrm{NH}-$	531.6 eV (531.6 eV)	$\mathrm{S}{=}\boldsymbol{O}$
			533.2 eV (533.3 eV)	$\mathrm{C}-\boldsymbol{O}-\mathrm{C}$
			539.2 eV (539 eV)[b]	shake-up
N1s	399.8 eV (399.8 eV)	$-\mathrm{CO}\boldsymbol{N}\mathrm{H}-$		
$\mathrm{S2p}_{1/2}$ $\mathrm{S2p}_{3/2}$			168.7 eV (168.7 eV)[b]	$\mathrm{C}-\boldsymbol{S}$, $\boldsymbol{S}{=}\mathrm{O}$
			167.4 eV (167.6 eV)	$\mathrm{C}-\boldsymbol{S}$, $\boldsymbol{S}{=}\mathrm{O}$
			174.3 eV (174 eV)[b]	shake-up

[a] Values shown in parentheses are from the literature.[35] [b] Values read from the spectrum given in the literature.

Table 3. Surface Composition of Two Component Polymers

	C[b]	O[b]	N[b]	S[b]
aPA	84.3	9.7	6.0	0.0
nf-PSU	83.7	13.5	0.0	2.8
	(84.4)[a]	(12.5)[a]	(0.0)[a]	(3.1)[a]

[a] Values shown in parentheses are those calculated from the chemical structure. [b]Atomic %.

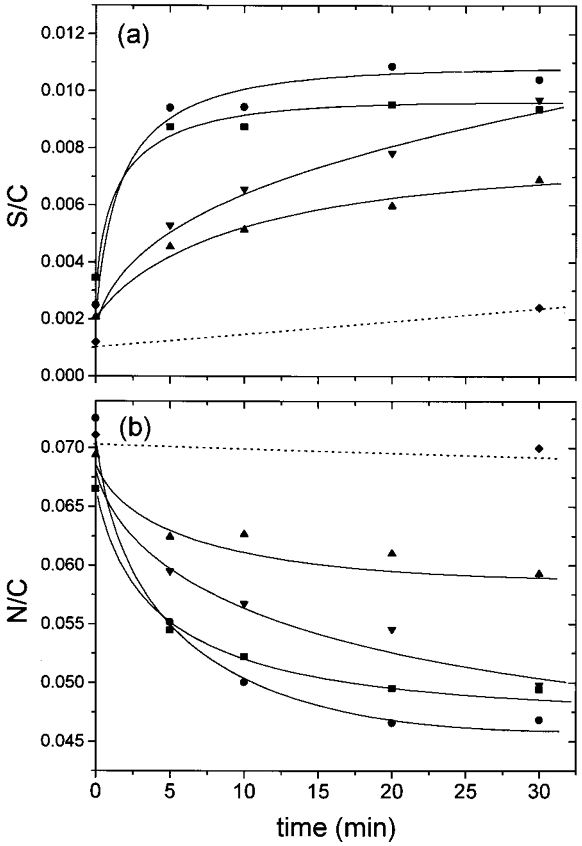

Figure 7. Changes in (a) the S/C atomic ratio and (b) the N/C atomic ratio of the exposed interface against annealing time, when bilayer films were heated at 200 °C for a given time and unreacted PSU chains were removed by solvent. The functionality of reactive PSU was fixed at 55 μmol/g: (●) aPA/PSU-ω-PAH; (■) aPA/PSU-*g*-MAH; (▼) aPA/PSU-ω-EP; (▲) aPA/PSU-ω-TRI; (◆) aPA/nf-PSU].

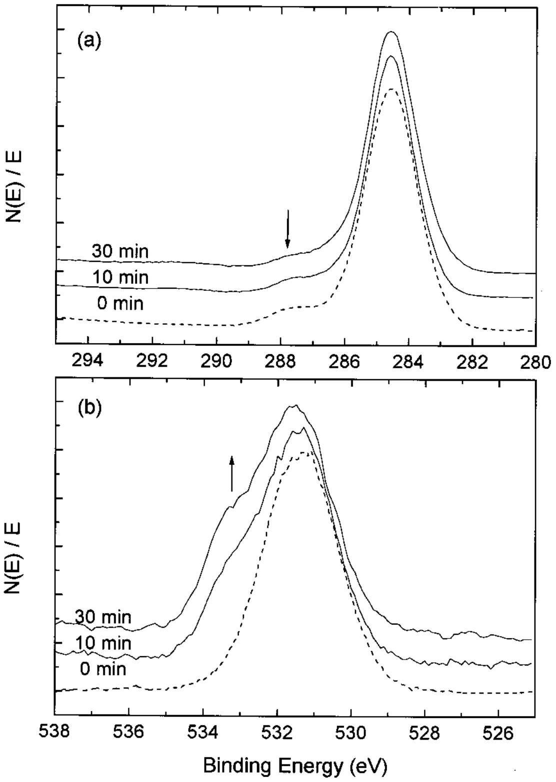

Figure 8. Changes in (a) the C 1s and (b) the O 1s photopeaks in the PSU-ω-EP/aPA system with increase in annealing time at 200 °C, respectively.

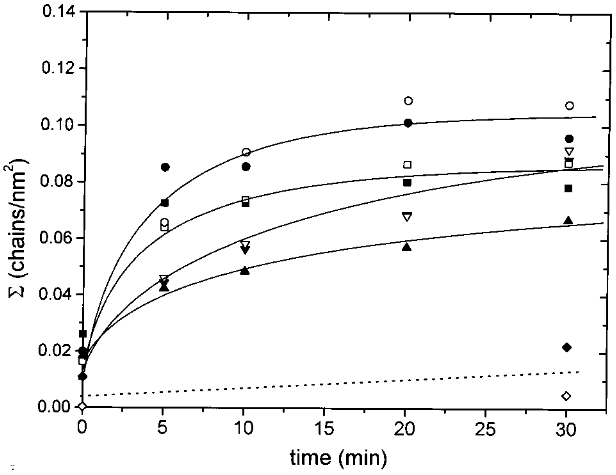

Figure 9. Areal density of copolymers formed in situ at the interface, Σ, when the bilayer specimens were heated at 200 °C for a given time. The values indicated by closed and open marks were estimated from the S/C ratio and the N/C ratio, respectively. All symbols are the same as those used in Figure 7.

amide group of aPA and S=O and −O− groups of PSU, which makes the complete removal of the unreacted PSU chains difficult.

Coupling Model and Kinetic Equations. Since the diffusion of reactive chains moving to the interface can be considered to be almost identical in all systems with similar molecular weights, the results observed in Figure 9 clearly indicates that the coupling kinetics are reaction-controlled. In other words, the diffusion of the reactive chains to the interface is much faster than the reaction between the reactive pairs located at the interface. This result demonstrates that the theory developed by Fredrickson's group[21,22] is not applicable in our system, in which kinetics are predicted to be diffusion-controlled in the whole time scale.

The kinetics of the present coupling reaction were further analyzed using the model proposed in our previous work.[28] The model makes five assumptions:

1. A flat interface is formed between the polymers.
2. The copolymers formed by the reaction stay stably at the interface.
3. The coupling reaction proceeds two-dimensionally on the interface place.
4. A monolayer-like quantity develops at the interface.
5. There is a saturation areal density of copolymers (Σ^*), at which the reaction is terminated.

The reaction kinetics were examined by carrying out first-order (Figure 10a) and second-order (Figure 10b) analyses, based on the assumption that the reaction rate would vary with the amount of vacant sites available for the further reaction, ($\Sigma^* - \Sigma$). The Σ value averaged from those obtained from the S/C and N/C ratios was used in this figure. The results clearly showed that the

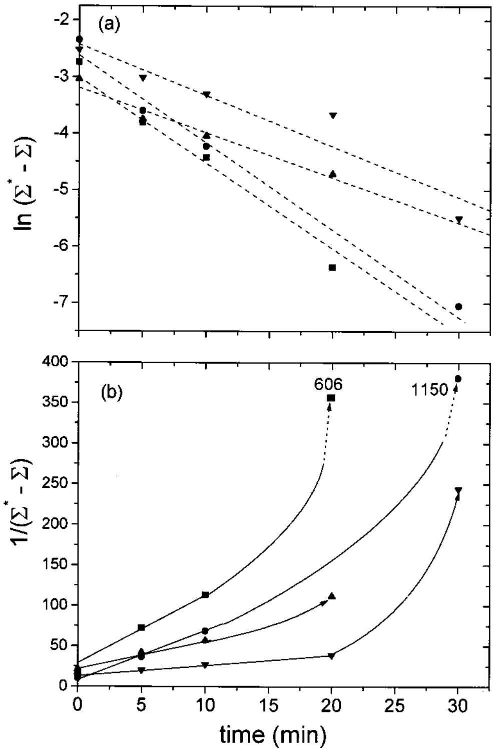

Figure 10. (a) First-order plot and (b) second-order plot of the data shown in Figure 9. All symbols are the same as those used in Figure 7. The Σ value averaged from those obtained from the S/C and N/C ratios was used in this figure.

coupling reaction apparently followed first-order kinetics in $(\Sigma^* - \Sigma)$. When the supply of both reactive groups is sufficient at the interface in the reaction time scale, the reaction rate, r_{AB}, would vary proportionally to the vacant sites available for the reaction, resulting in the pseudo-first-order kinetics in $(\Sigma^* - \Sigma)$, as shown by the next kinetic equations

$$r_{AB} = k_{AB}(C_A - C_{AB})(C_B - C_{AB})(\Sigma^* - \Sigma) \quad (4)$$

$$r_{AB} = k_{AB}C_AC_B(\Sigma^* - \Sigma) \quad (C_A, C_B \gg C_{AB}) \quad (5)$$

where k_{AB} is the rate constant, C_{AB} is the concentration of copolymers formed at time t, and C_A and C_B are the concentration of A and B reactive groups prior to the reaction, respectively. Here the values of C_A and C_B can be considered as the numbers of reactants per unit interfacial area located within the distances of $2\sqrt{D_At_c}$ and $2\sqrt{D_Bt_c}$, respectively, from the interface, where D_A and D_B are the self-diffusion coefficient of the reactive chains carrying the reactants, A and B, respectively, and t_c is the reaction time needed to reach Σ^*.

Padwa et al. investigated the reaction kinetics between primary amine and cyclic anhydride in solutions of LMW/LMW, LMW/polymer, and polymer/polymer model systems and reported the reaction rate constants, in which the reaction was considered to have two steps: the first step being amic acid formation and the second step being imide formation.[18] They concluded that the second step was rate-determining. The assignment of the reaction order was not easy in the second step so that the rate constants calculated from the second-order plot in the initial reaction stage were used for their discussion.

Apparent Rate Constant (*k*) and Saturation Areal Density of Copolymers (Σ*): On the basis of eq 5, the apparent rate constant, k, and the saturation areal density of copolymers, Σ^*, for the different reactive pairs were obtained and listed in Table 4. Here the apparent rate constant, k, was defined as $k_{AB}C_AC_B$ in eq 5, which was obtained both by the first-order fit in Figure 9 and by the slope of the straight lines in Figure 10a. Although the latter method is a common method to estimate the rate constant, it neglects Σ values larger than the Σ^* value in the process of calculation, so that k was also estimated from the first-order fit in Figure 9 in order to use all of the limited data.

Table 4. Apparent Rate Constant, *k*, and Saturation Areal Density of Copolymers, Σ*, of Different Reactive Pairs at 200 °C

	k (s^{-1}) obtained from Figure 9	k (s^{-1}) obtained from Figure 10a	Σ^* (chains/nm^2)
aPA/PSU-*ω*-PAH	0.0038	0.0026	0.103
aPA/PSU-*g*-MAH	0.0032	0.0025	0.085
aPA/PSU-*ω*-EP	0.0017	0.0015	0.094
aPA/PSU-*ω*-TRI	0.0017	0.0013	0.066

It was concluded that k decreased in the order PSU-*ω*-PAH > PSU-*g*-MAH ≫ PSU-*ω*-EP ≥ PSU-*ω*-TRI in the reaction with aPA. These results demonstrated that two anhydride groups possessed much larger reaction rates compared to the epoxide and triazine groups, reaching their Σ^* values faster.

On the contrast, Σ^* decreased in the order PSU-*ω*-PAH > PSU-*ω*-EP > PSU-*g*-MAH > PSU-*ω*-TRI. If the molecular architecture of the copolymers illustrated in Figure 3 is taken into consideration, it can be seen that the magnitude of Σ^* might be affected by the area occupied by a single copolymer chain located at the interface at saturation. For example, the most compact linear copolymer formed between one aPA chain and one PSU-*ω*-PAH chain showed the largest Σ^* value, whereas the most bulky branched copolymer formed between two aPA chains and one PSU-*ω*-TRI chain resulted in the lowest Σ^* value. In the PSU-*ω*-EP/aPA system a small amount of triblock copolymers might have contributed to the decrease in the Σ^* value.

Norton et al. reported that the saturation grafting density of PS chains terminated by the COOH group onto an amine-rich epoxy surface, $\Sigma_g{}^*$, changed with N^{-1}, where N was the degree of polymerization of PS chains.[10] In the present study, the relationship $\Sigma_g^* \sim N^{-1}$ will be clearly invalid because of the different architectures of the copolymers. However, if the relationship is rewritten as $\Sigma_g^* \sim R_g{}^{-2}$ since $N \sim R_g{}^2$, where R_g is the radius of gyration of the grafted PS chains, the relationship clearly indicates that the Σ_g^* is determined by the interfacial area occupied by one grafted chain. Thus, it is reasonable to predict that the Σ^* would be determined by the interfacial area occupied by one copolymer chain at saturation, when there is a sufficient supply of the reactants at the interface (C_A, $C_B \gg C_{AB}$).

Last, it should be pointed out that the conformation of the copolymer chain at saturation should be important for the determination of the end point of the reaction. It is reported that the copolymer conformation at the interface changes from a relaxed to an extended form with an increase in the Σ value.[39] Our analysis on the PSU/aPA and other reactive polymer systems[28] indicated that there was no clear discontinuity in kinetics caused by the conformational change. The increase in the Σ value agreed well with the first-order fit in the whole time scale.

All these examples indicate that Σ^* is a valid parameter for analyzing the kinetics of copolymer formation in immiscible polymer systems. The quantity is readily measurable experimentally and has a definite physical meaning, being probably related to the interfacial area occupied by one resultant copolymer chain at saturation.

Conclusions

The coupling reaction at the immiscible polymer–polymer interface was investigated using bilayer films composed of amorphous polyamide (aPA) and polysulfone (PSU). The model we proposed in the previous paper[28] could explain the kinetics, with the overall coupling reaction kinetics being well-described by a pseudo-first-order process in ($\Sigma^* - \Sigma$), the amount of vacant sites available for further reaction at the interface. The time dependence was described by an exponential function $\Sigma \sim -\exp(-t)$. By employing various kinds of reactive PSUs incorporating different functional groups, it was found that the apparent rate constant (k) and the saturation areal density of the copolymers formed at the interface (Σ^*) decreased in the following order:

$$k\text{: PSU-}\omega\text{-PAH} > \text{PSU-}g\text{-MAH} \gg \text{PSU-}\omega\text{-EP} \geq \text{PSU-}\omega\text{-TRI}$$

$$\Sigma^*\text{: PSU-}\omega\text{-PAH} > \text{PSU-}\omega\text{-EP} > \text{PSU-}g\text{-MAH} > \text{PSU-}\omega\text{-TRI}$$

Thus, k was larger for the two anhydride groups, PAH and MAH, and Σ^* became larger in reactions resulting in a copolymer, which could take a conformation with smaller interfacial area at saturation. This implies that Σ^* might be determined by the packing efficiency of copolymers at saturation.

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