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Evolution of the Interfacial Tension between Polydisperse "Immiscible" Polymers in the Absence and in the Presence of a Compatibilizer

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ABSTRACT: The interfacial tension σ between two polyisobutylenes (PIB) of dissimilar polydispersity and two polydisperse samples of poly(dimethylsiloxane) (PDMS) was measured as a function of time by means of a pendent drop apparatus at different temperatures ranging from 30 to 110 °C. In addition to three of the four possible binary blends, the time evolution of σ was also determined for one ternary system, where the PIB phase contained 0.03 wt % of a diblock copolymer poly(isobutylene-*b*-dimethylsiloxane). The pronounced decrease of σ with advancing time, observed in all cases, is attributed to the migration of the interfacially active lower molecular weight components of the homopolymers and of the compatibilizer into the interphase. Several days are normally required until σ becomes constant. These time independent values are not considered as equilibrium data, but accredited to stationary states. A kinetic model is established for $\sigma(t)$, which enables a detailed investigation of the rates of transport of the different migrating species of average molar mass of M. Its application to the present data discloses that the characteristic times τ of their diffusion depend on M^d, where the estimated d values vary between 2.9 and 5.1. The modeled dependence of τ on the viscosities of the coexisting phases suggests that the activation energies for τ should be found somewhere between the activation energies for the viscous flow of these bulk phases. The experimental observations corroborate this postulate.

1. Introduction

Interfacial equilibria are rapidly established if two low molecular weight liquids get in touch with each other. For solutions of polymers in single solvents, this process requires considerably more time as has for instance been demonstrated by means of temperature jump experiments.[1] Furthermore, we encounter an additional difficulty, which results from the polydispersity of most macromolecular compounds. This feature has far reaching consequences[2] for the equilibrium interfacial tension σ between coexisting phases of demixed polymer solutions of different overall composition. Because of the fractionation associated with phase separation, the work required to produce new interface depends on the overall composition of the mixture.

The situation turns out to be still more complicated for polymer blends due to the normally very high viscosities of the components of the mixtures. For such systems, the transport processes take place so slowly that it becomes comparatively easy to study the kinetics with which time independent interfacial tensions are established. Literature reports on this topic concern the effect of random copolymer additives on the interfacial tension between incompatible polymers,[3] diffusion effects on the interfacial tension of polymer blends,[4] the segregation dynamics of block copolymers to immiscible polymer blend interfaces,[5] and differences in the efficiency of a compatibilizer depending on the bulk phase to which it is added.[6] In the first three papers the constant σ values reached after sufficient time of waiting are interpreted as equilibrium data. On the basis of the experimental observations described in ref 6, the time independent interfacial tensions reached in these experiments were attributed to the establishment of stationary states and not to equilibria.

In this work, we are checking whether the ideas developed in the course of a study on the efficiency of compatibilizers and the knowledge on the time dependence of the interfacial tension for such systems[3,6] can be used to reach a better understanding of the pronounced time dependence of σ in the case of polydisperse polymer samples. To this end, we have measured the interfacial tension by means of the pendent drop method as a function of time at different temperatures for three binary blends of polyisobutylene (PIB, matrix) and poly(dimethylsiloxane) (PDMS, droplet) and one ternary blend where a diblock copolymer P(IB-*b*-DMS) was added to the PIB phase. For this investigation we have fractionated PIB so that we could study two samples with identical M_n values but different polydispersities. These experimental results where then evaluated with respect to the transport rates of the different blend components by means of a kinetic model for the stationary state interfacial tensions σ_s. Several studies on polydispersity effects have been published.[2,7,8]

2. Experimental Section

2.1. Materials. Poly(dimethylsiloxane) (PDMS) was supplied by Wacker, Munich, Germany, polyisobutylene (PIB wide) by BASF, Ludwigshafen, Germany, and a diblock copolymer (COPO), consisting of IB and DMS units, supplied by Polymer Source Inc., Montreal, Canada. PIB narrow was obtained via continuos polymer fractionation[9,10] of PIB wide. The molecular weights were determined by means of gel permeation chromatography, using toluene as solvent and applying an universal calibration by means of polystyrene standards. The characteristic data of the different polymer

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Table 1. Molar Masses and Polydispersities of the Polymers

material	M_n/kg mol^{-1}	M_w/kg mol^{-1}	M_w/M_n
homopolymers			
PDMS 87n	87.00	153.00	1.76
PDMS 55n	55.00	87.00	1.58
PIB wide	0.95	2.46	2.59
PIB narrow	0.99	1.74	1.76
diblock copolymer (COPO)			
P(IB 6.5-*b*-DMS 5.5)	12.00	13.80	1.15

Table 2. Densities of the Homopolymers and Their Temperature Dependence

PDMS 87n	ρ/g cm^{-3} = 0.99345 − 8.8 × 10^{-4}t/°C
PDMS 55n	ρ/g cm^{-3} = 0.99075 − 8.5 × 10^{-4}t/°C
PIB wide	ρ/g cm^{-3} = 0.90583 − 5.5 × 10^{-4}t/°C
PIB narrow	ρ/g cm^{-3} = 0.90401−5.5 × 10^{-4}t/°C

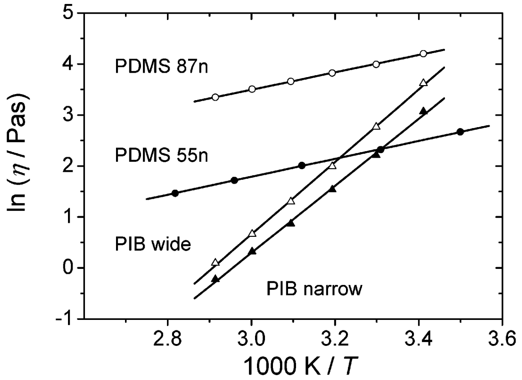

Figure 1. Temperature dependence of the zero shear viscosities of the pure polymer melts.

samples are shown in Table 1; the numbers in the abbreviations give the number-average molar mass in kilograms per mole. The information about the diblock copolymer stems from the supplier.

The densities of the polymers were determined as a function of temperature by means of a commercialized apparatus (DMA 48, Paar Physica, Graz, Austria) between 20 and 70 °C in steps of 10 °C. These results are listed in Table 2.

Zero shear viscosities, η, of the pure homopolymers were measured with the stress controlled rheometer, AR 1000 (TA Instrument) using a cone and plate geometry. The measurements were carried out from 20 to 70 °C in intervals of 10 °C. The results are depicted in Figure 1 in terms of an Arrhenius diagram.

2.2. Methods. The interfacial tension σ between the two coexisting liquid phases of the binary or ternary systems was determined by means of the pendent drop method.[11,12] The apparatus used for that purpose has already been described in detail.[13] The measurements were carried out from 30 to 110 °C in 10 °C intervals. The compound of larger density (PDMS) forming the droplet is highly incompatible with the matrix phase (PIB). In the case of the ternary systems the additive was given to the matrix phase (PIB) because it is very sparingly soluble in PIB but practically insoluble in PDMS. The typical experimental errors of the interfacial tension measurements are estimated to be 5%.[3]

3. Theoretical Background

3.1. Stationary States. The interfacial tension between two macromolecular liquids depends on the chain lengths of the components. Keeping the molar mass of one polymer constant and varying that of the other this dependence can be formulated[14] as

$$\sigma = \sigma_\infty - \frac{C}{{M_n}^z} \tag{1}$$

where C and z are constants. The fact that the interfacial tension is less for low molecular weight polymers than for high molecular weight ones has far-reaching consequences for the interfacial behavior of real polymer blends. As a result of this situation, the short chain components of broadly distributed samples will migrate into the interphase to reduce σ and consequently the Gibbs energy of the entire system

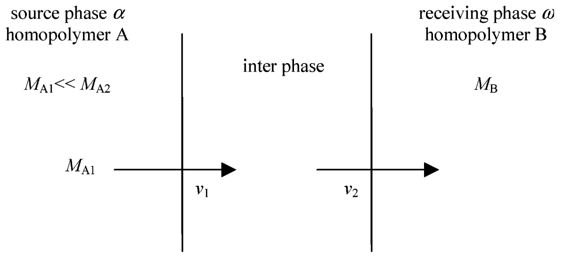

Figure 2. Scheme demonstrating the establishment of a stationary interphase concentration for M_{A1}, the lower molecular weight component of the homopolymer A

From experiments with ternary systems consisting of two incompatible polymers and a block copolymer as compatibilizer, it has become obvious that the time independent information on the interfacial tension does not refer to equilibrium conditions, but must be interpreted in terms of stationary states.[6] This situation is evidenced by the observation that these constant σ values depend on the phase to which the copolymer was added. The lowest interfacial tension was reached if the copolymer was added to both phases. In case only one of the coexisting phases contains the additive at the beginning of a measurement, this indepdence of the interfacial tension on time is due to the migration of the compatibilizer from the source phase into the interphase and from there into the receiving phase. With the present binary mixtures of polymolecular homopolymers the situation is very similar: The lower molecular weight components of the polymers A and B migrate into the interphase and move on into the opposite phase to the extent their solubility in the receiving phase admits it. Owing to the high viscosity of polymer liquids that migration can require considerable time before the measurements become time independent. In the next section, we will be modeling the kinetics of these processes.

This situation is in the following part discussed in more detail by means of a ternary model blend consisting of two molecularly uniform species A1 and A2 of a homopolymer A (with the molar masses $M_{A1} \ll M_{A2}$) plus one kind of molecule of homopolymer B (with the molar mass M_B). For that purpose, we distinguish between three phases as shown in Figure 2, namely the two bulk phases containing the homopolymers and a transition phase (interphase) between them.

To establish equilibrium, the lower molecular weight homopolymer A1 will migrate from the bulk phase A (source phase α) into the interphase and from there (to the extent the interaction between A and B segments permits) into the bulk phase B (receiving phase ω). If the rates of transport v_1 and v_2 turn out to be identical, the concentration x of the lower molecular weight species of A in the transition phase becomes independent of time before equilibrium is reached. To distinguish the interfacial tensions from equilibrium, data they are denoted as σ_s (stationary) instead of σ. The fact that x and the interfacial tension are closely interrelated permits a kinetic analysis of the evolution of interfacial tension in the case of molecularly nonuniform samples.

Assuming that the concentration x_α of M_{A1} in the source phase remains constant and that in the receiving phase negligibly small during the time slice of interest, as compared with the equilibrium concentration, we can formulate the time dependence of x as

$$\frac{dx}{dt} = k_1(x_\alpha - x) - k_2 x \tag{2}$$

where the first term is v_1 and the second term v_2; k_1 and k_2 are the corresponding rate constants. As the rates of transport into the interphase and out of it become identical ($dx/dt = 0$), this relation yields the following expression for x_s, the stationary value of x

$$x_s = \frac{k_1 x_\alpha}{k_1 + k_2} \tag{3}$$

Inserting x_α from eq 3 into eq 2 and redefining the independent variable as $(x_s - x)$, we end up with the following simple relation

$$-\frac{d(x_s - x)}{dt} = (k_1 + k_2)(x_s - x) \tag{4}$$

from which we obtain after integration, substitution of the integration constant and rearrangement

$$x = x_s + (x_o - x_s)e^{-(k_1+k_2)t} \tag{5}$$

At the reference time ($t = 0$) the value of x is x_o and at sufficiently long times x approaches the steady-state value x_s. For the present example x rises steadily starting from x_o, the minimum value established in the interface immediately after its formation.

Under the reasonable assumption[6] that the interfacial tension decreases as the accumulation of the favorable component A1 in the interphase advances, i.e., postulating to a first approximation a proportionality between dx and $d\sigma$ for the present situation, where we are far from complete coverage of the interface by the preferentially adsorbed component, we can rewrite eq 5 as

$$\sigma = \sigma_s + (\sigma_o - \sigma_s)e^{-(k_1+k_2)t} \tag{6}$$

where σ_o stands for the interfacial tension measured at time zero and σ_s represents the steady-state value.

The next obvious question reads how the rate constants k_i depend on the properties of the blend components. The central influencing variables are the thermodynamic driving forces for the diffusion of the lower molecular weight material out of the source phase α into the interphase and from there into the receiving phase ω, the chain length of the migrating species (i.e., their mobility), and the viscosities of the two bulk phases. In view of the fact that the thermodynamic details are in most cases not available, these contributions are, together with other system specific parameters, incorporated into the factors k_1^* and k_2^*. Under these assumptions we obtain the following relations

$$k_1 = \frac{k_1^*}{{M_{A_1}}^d \eta_\alpha} \tag{7}$$

and

$$k_2 = \frac{k_2^*}{{M_{A_1}}^d \eta_\omega} \tag{8}$$

where the particular manner in which the mobility of the migrating species, i.e., its rate constants, increases as their molar mass becomes less is expressed by means of the yet unknown exponent d. The viscosities of the source phase is denoted as η_α and that of the receiving phase as η_ω.

If we introduce the maximum achievable reduction of the interfacial tension as

$$\Delta\sigma = \sigma_o - \sigma_s \tag{9}$$

and replace the rate constants by their more descriptive inverse, the characteristic times τ, we can rewrite eq 6 as

$$\sigma = \sigma_s + \Delta\sigma e^{-t/\tau} \tag{10}$$

where

$$\tau = {M_{A_1}}^d \left(\frac{k_1^*}{\eta_\alpha} + \frac{k_2^*}{\eta_\omega}\right)^{-1} \tag{11}$$

From this relation, it becomes immediately obvious that the characteristic time of the attainment of steady states decreases (quicker transport) as the chains become shorter and as the viscosities of the bulk phases fall.

Real polymer blends are normally made up of two components, which both exhibit a broad molecular weight distribution, and often a compatibilizer is added to one of the bulk phases only. This means that the short chains of A and B and an additive C will migrate into the interphase until a steady state is reached. Under the assumption that each of these processes contributes individually to the total reduction of the interfacial tension down to the stationary value σ_s according to

$$\Delta\sigma = \sigma_o - \sigma_s = \Delta\sigma_{s,A} + \Delta\sigma_{s,B} + \Delta\sigma_{s,C} \tag{12}$$

we can generalize eq 10 for the present purposes and obtain

$$\sigma = \sigma_s + \Delta\sigma_{s,A}e^{-t/\tau_A} + \Delta\sigma_{s,B}e^{-t/\tau_B} + \Delta\sigma_{s,C}e^{-t/\tau_C} \tag{13}$$

This equation is in its mathematical form identical with an empirical relation reported earlier[3], which describes the time dependence of σ for a system of the type homopolymer A/homopolymer B/poly(A-*ran*-B).The authors explained this behavior assuming the existence of two processes. The first one consists of the attainment of the hydrodynamic equilibrium and the second process concerns the diffusion of the copolymer to the interface. Equation 13 enables the determination of the characteristic times for the migration of the different components into the interphase by means of the measured $\sigma(t)$. Furthermore, it is possible to quantify the individual contributions of the different migrating components to the overall reduction of interfacial tension from the different $\Delta\sigma_{s,i}$ values, if one knows the exact time at which the interface between the two liquid phases is formed and if the droplet relaxes sufficiently fast into its equilibrium shape.

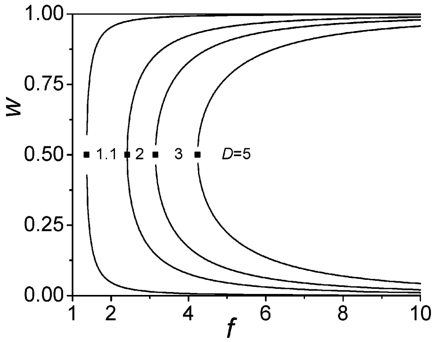

Figure 3. Combinations of the disproportionation factors *f* and weight fractions *w* of the two components of a model blend that are required to yield the polydispersity indices *D* indicated in the graph

3.2. Simulation of Polydispersity. The considerations of the previous chapter were based on the substitution of a polymer with broad molecular weight distribution by a mixture of two individual species (pseudocomponents) of different molar mass. To apply that concept adequately to real polymer blends, we need to find out how their polydispersities can be modeled by properly choosing the molar masses of the pseudocomponents and their mixing ratio.

For the polydispersity index D, the ratio of the weight, and of the number-average of the molar mass, the following general equations hold true

$$D = \frac{M_w}{M_n} = \sum w_i M_i \sum \frac{w_i}{M_i} \tag{14}$$

where w_i stands for the weight fraction of component i with the molar mass M_i. To model polydispersity we start with a molecularly uniform polymer species with the molar mass M (for instance one of the average molar masses of the real sample) and "disproportionate" them it into two components according to M/f and $M\,f$ where $f > 1$ is a constant factor. Denoting the weight fraction of the shorter chains by w eq 14 yields the following expression (no longer containing M) for the interrelation between the polydispersity index D and the equivalent blend of only two polymer species

$$D = \frac{(f^2 - w(f^2 - 1))(w(f^2 - 1) + 1)}{f^2} \tag{15}$$

By solving this equation with respect to w, we can calculate how much of each component is needed for a given value of f in order to model a certain polydispersity. This relation reads

$$w = \frac{1}{2} \pm \frac{\sqrt{f^4 + f^2(2 - 4D) + 1}}{2(f^2 - 1)} \tag{16}$$

Figure 3 shows how this dependence looks like for different polydispersities

It is obvious that there exist infinitely many combinations of molar masses and mixing ratios to model a certain polydispersity. The least factor f is required for one by one mixtures; under this condition the square root of eq 16 becomes zero. and we obtain

$$f_{\min} = [2D - 1 + 2\sqrt{D(D - 1)}]^{0.5} \tag{17}$$

3.3. Activation Energies. According to eq 11, the characteristic times τ for the transport of a given blend component from the source phase into the receiving phase increases with the viscosities of these phases. The temperature dependencies of τ and of η should consequently be interrelated. For the activation energies, we write

$$E_X^{\ddagger} = R\,\frac{d \ln X}{d(1/T)} \tag{18}$$

where X stands for τ or η. Under the simplifying assumption that practically all temperature influences go into the characteristic times and viscosities, i.e., neglecting that k^* might also vary slightly with temperature, we obtain the following simple interrelation upon the differentiation of eq 11

$$E_\tau^{\ddagger} = \varpi_\alpha E_{\eta_\alpha}^{\ddagger} + \varpi_\omega E_{\eta_\omega}^{\ddagger} \tag{19}$$

where the extent $\varpi_\alpha = 1 - \varpi_\omega$ to which the activation energies for the viscous flow of the two coexisting polymer melts contribute to the activation energy of diffusion depends on the kinetic constants of the individual process (cf. Figure 2) and on the viscosities as follows:

$$\varpi_\alpha = \frac{\dfrac{k_1^*}{\eta_\alpha}}{\dfrac{k_1^*}{\eta_\alpha} + \dfrac{k_2^*}{\eta_\omega}} = 1 - \varpi_\omega \tag{20}$$

3.4. The Exponent *d*. To obtain information on the influences of chain length, we need to know the behavior of at least two samples differing sufficiently in the molar mass of the migrating species under else as similar conditions as possible. If we introduce the index I for one species and II for the other, we obtain the following relation from eq 11

$$\frac{\tau_I}{\tau_{II}} = \left(\frac{M_I}{M_{II}}\right)^d \frac{\left(\dfrac{k_1^*}{\eta_\alpha} + \dfrac{k_2^*}{\eta_\omega}\right)_{II}}{\left(\dfrac{k_1^*}{\eta_\alpha} + \dfrac{k_2^*}{\eta_\omega}\right)_{I}} \tag{21}$$

where the k values are the only unknowns for the calculation of d. The characteristic times of the two samples and the viscosities of the different melts are measured quantities and M_I/M_{II} can estimated as follows. For the same molecular weight distributions this ratio is simply set equal to the ratio of the average molar masses of the samples and in the case of dissimilar molecular weight distributions it is calculated by means of the minimum disproportionation factor $f_{\min}$ (17) required for the modeling of the different polydispersities as

$$\frac{M_I}{M_{II}} = \frac{f_{\min\,II}}{f_{\min\,I}} \tag{22}$$

Furthermore, we eliminate one of the two kinetic constants with the aid of eq 20 and insert

$$k_1^* = k_2^* \frac{\eta_\alpha}{\eta_\omega} \frac{\varpi_\alpha}{\varpi_\omega} \qquad (23)$$

into eq 21. Logarithmizing the resulting relation yields

$$\log \frac{\tau_\mathrm{I}}{\tau_\mathrm{II}} = d \log \left(\frac{M_\mathrm{I}}{M_\mathrm{II}}\right) + \log \left(\frac{k_2^{*\mathrm{II}}\, \varpi_\omega^\mathrm{I}}{k_2^{*\mathrm{I}}\, \varpi_\omega^\mathrm{II}}\right) \qquad (24)$$

Under the reasonable assumption that the k_2^* values do not depend on the molecular weight of the migrating species, we are now in the position to assess the value of the exponent d.

4. Results and First Analysis

The time evolution of σ was fitted according to eq 13. For the kinetic analysis it is important to know that the hydrodynamic equilibrium is reached very rapidly (because of the low viscosities of the present blend components the required time lies typically on the order of seconds)[15] and need not be taken into account in the present context. To facilitate the allocation of the τ values to the components of the mixture, the receiving phase is specified in the graphs in Figures 6, 7, and 10. Furthermore, these characteristic times are already now appointed: According to the much lower molar mass of PIB, as compared with that of PDMS, τ_1 should refer to PIB and τ_2 to PDMS. The assignment of τ_3 to the copolymer additive follows from the comparison of the results for the ternary and for the binary system.

4.1. Binary Systems. Figure 4 shows the stationary interfacial tensions between two homopolymers of non-negligible molecular polydispersity, which are at different temperatures reached after sufficient time (cf. for instance Figure 5). In this context, it is interesting to note that the mutual miscibility of PIB and PDMS is negligible according to previous measurements[16] with considerably lower molecular poly(dimethylsiloxane)s. It is obvious that the PIB sample with the narrower molecular weight distribution leads to considerably larger σ_s values as compared with the sample of higher polydispersity, despite identical number-average molar masses. The changes in σ_s resulting from a reduction in the M values of PDMS from 87 to 55 kg/mol are so small that they almost remain within experimental error.

How the stationary interfacial tensions shown in Figure 4 are reached as time proceeds is depicted in Figure 5 for one temperature and two systems differing only in the polydispersity of the PIB sample.

The information concerning the characteristic times of transport obtained from graphs of the type shown above is presented in Figure 6. The data of part a demonstrate that the short chain components of the broadly distributed PIB migrate much more rapidly into the PDMS phase than that of the sample with the narrower molecular weight distribution. This result is in agreement with the consideration dealing with the simulation of polydispersity effects. The findings shown in part b testify to the role of the viscosity of the receiving phase. The migration of PDMS molecules into PIB of larger polydispersity requires more time because of the higher viscosity of this PIB sample (cf. Figure 1), as compared with that of lower polydispersity.

We are now considering the diffusion of the short chains of PIB wide into PDMS samples of different average molar mass (Figure 7, part a). The results are totally analogous to that obtained for the transport of the lower molecular weight components of PDMS 87 into PIB of different polydispersity. Also of interest are the effects of the differences in the average molar mass of PDMS for the diffusion of their respective lower molecular components into PIB wide (Figure 7, part b). In this case, the effects resulting from the differences in the viscosities of the components and in the molar mass of the diffusing species act in the same direction and the τ values become particularly diverse.

Some fundamental features become immediately obvious from the present results. Most remarkable is the rapid approach of the stationary state for the PIB sample with the broad molecular weight distribution as compared with that of the narrow molecular weight distribution, despite practically identical M_n values. The

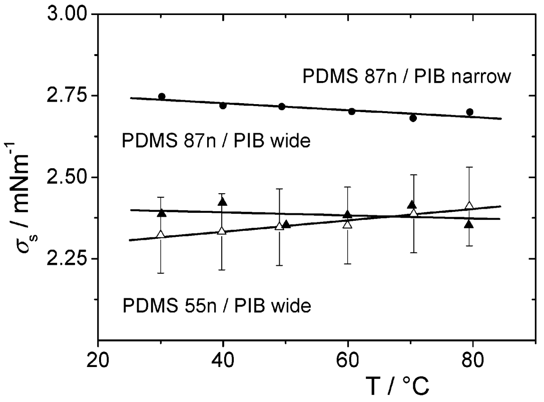

Figure 4. Time independent interfacial tension as a function of temperature for the different binary blends. Due to the large scale, the typical errors (±5%) appear considerable.

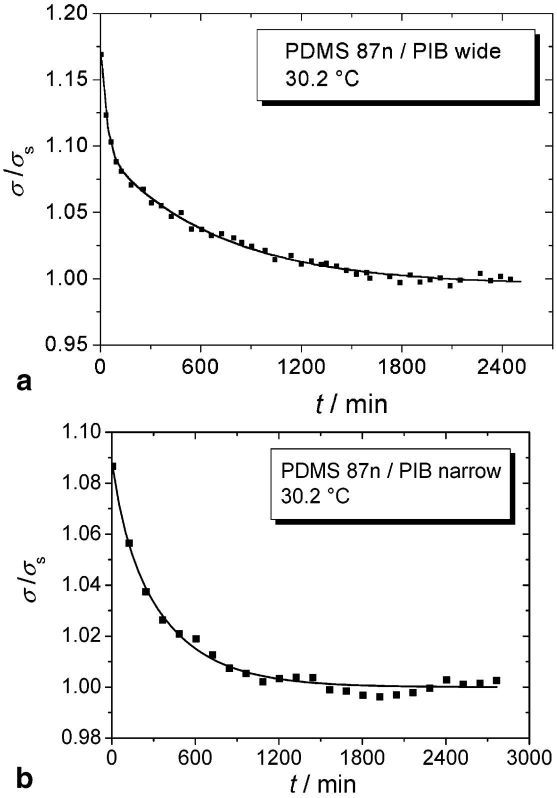

Figure 5. Comparison of the evolution of interfacial tension, normalized to its limiting value at infinite time, for blends of a given sample of PDMS with either broadly (a) or narrowly (b) distributed PIB at the indicated temperature. The curves are adjusted to the experimental data according to eq 13.

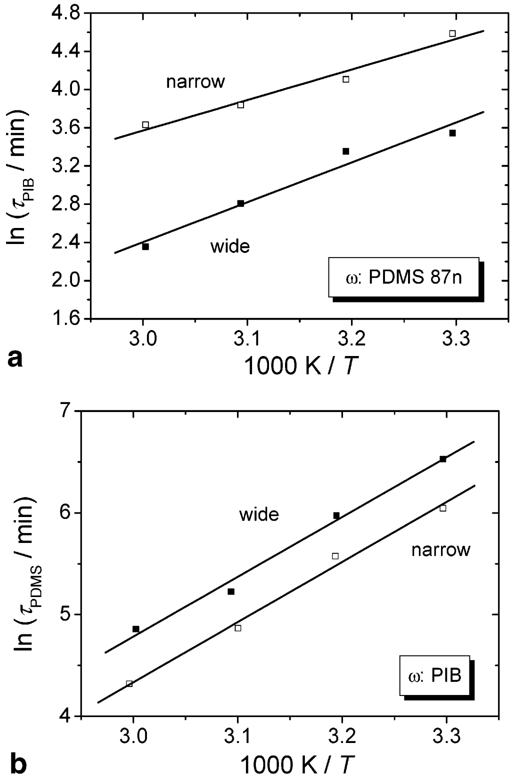

Figure 6. τ_{PIB} (a) and τ_{PDMS} (b) calculated according to eq 13 from the time evolution of the interfacial tension for blends of PDMS 87n with PIB of either wide or narrow molecular weight distribution as a function of temperature. The receiving phases ω are indicated in the boxes.

characteristic times for the migration of the low molecular weight components of PIB range from approximately 10 min (wide, 60 °C) to 1.5 h (narrow, 30 °C). For the PDMS samples under investigation, these times are considerably longer due to their much higher molar mass and consequently larger viscosities. They range from 16 min (PDMS 55, 60 °C) to approximately 11 h (PDMS 87, 30 °C). All these findings are in qualitative agreement with the predictions of eq 11 resulting from the model considerations concerning the establishment of stationary states. A quantitative evaluation of the data is presented in the last section.

4.2. Ternary Systems. The stationary state data for the interfacial tension between PDMS 87 and PIB wide containing 0.03 wt % COPO are depicted in Figure 8 as a function of temperature. The presence of the additive reduces σ_s to approximately half of the values observed for the binary system (Figure 4). The sign of the temperature influence on the interfacial tension remains unchanged, but the effect is larger for the ternary system. Because of experimental uncertainties, it remains unclear whether σ_s approaches a limiting value at high T. An example for the evolution of the interfacial tension with time is given in Figure 9.

The results of the examination of the time dependence of σ shown in Figure 9 with respect to the characteristic times of the different migration processes by means of eq 13 can be seen from Figure 10. At high temperatures the short chain components of PIB migrate approximately 1 order of magnitude more rapidly than that of PDMS and about 2 orders of magnitude quicker than the COPO. Upon a reduction of T, all processes become considerably slower and the differences in their rate less pronounced.

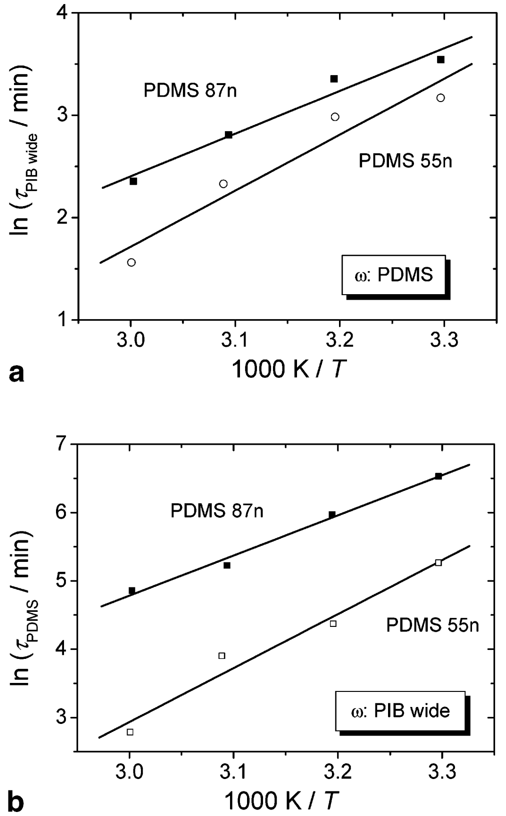

Figure 7. τ_{PIB} (a) and τ_{PDMS} (b) calculated according to eq 13 from the time evolution of the interfacial tension for blends of PDMS 87n or PDMS 55n with PIB of wide molecular weight distribution as a function of temperature. The receiving phases ω are indicated in the boxes.

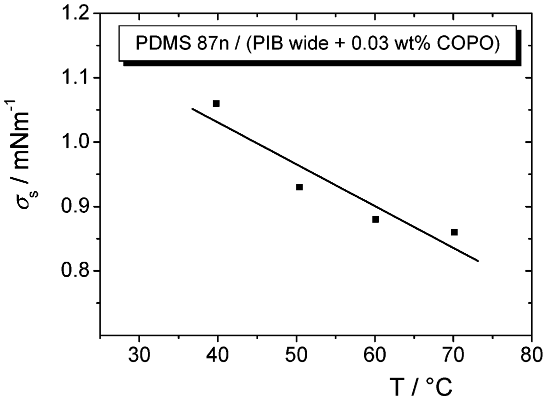

Figure 8. Time-independent interfacial tension as a function of temperature for system PDMS 87n/(PIB wide + 0.03 wt % COPO) as a function of temperature; the copolymer is initially exclusively contained in the PIB phase.

The characteristic times for the migration of the block copolymer can be compared with literature reports[5] on blends of polystyrene and PDMS where poly(styrene-*b*-dimethylsiloxane) diffuses into the interphase. Cho et al. explained the pronounced time dependence with three following stages: hydrodynamic equilibrium, diffusion of the copolymer to the interface, and attainment of equilibrium. The molar mass of this additive was very similar to that of the present COPO, but the viscosities of the homopolymers must have been orders of magnitude smaller due to their much lower molar masses and the high measuring temperature of 140 °C. From Figure 3 of ref 5, one can estimate from the second process a characteristic time of approximately 20 min, i.e., a value

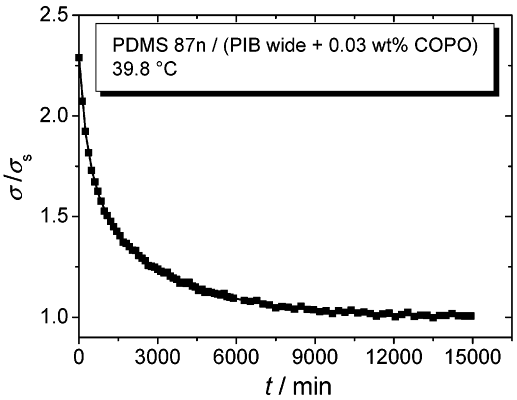

Figure 9. Evolution of interfacial tension, normalized to its limiting value at infinite time, for a mixture of PDMS 87n and PIB wide containing 0.03 wt % of COPO.

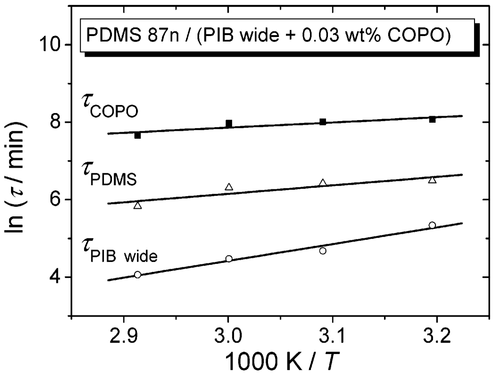

Figure 10. Characteristic times of the components of the ternary blend indicated in the graph as a function of temperature. For τ_{COPO} and for τ_{PIB} the receiving phase is PDMS 87n; for τ_{PDMS} it is PIB wide.

which is about 30 to 50 times smaller than in our case. In view of the role the viscosities of the bulk phases should according to the model calculations (eq 11) play for the values of τ, the differences appear reasonable.

The comparison of the results for the ternary system with the corresponding binary system reveals an interesting feature, namely a considerable slowing down of migration due to the presence of the compatibilizer. This effect is very pronounced for the diffusion of PIB out of the COPO-containing phase, where the τ values are at all temperatures reduced by a factor of approximately 8. However, even the transport of PDMS into the mixed phase is slowed by a factor of about 2 at the lowest temperature up to a factor of 4 at the highest temperature.

One can think of at least two explanations for this finding. Thermodynamic and hydrodynamic interactions between the short chain homopolymers with the corresponding blocks of the copolymer may slow diffusion. A more detailed analysis of these effects would require a treatment in terms of thermodynamics of irreversible processes. According to a less phenomenological interpretation, the reduced diffusion rates may be attributed to the accumulation of the block copolymer at the interface, which hinders the passage of the homopolymers.

5. Discussion

We are dealing with three questions in detail. (i) How do the results on the system PIB/PDMS reported in the literature[4] compare with the present findings? (ii) In which manner do the activation energies of the migration processes depend on the activation energies for the viscous flow of the two blend components? (iii) What is the actual value of the exponent d in eq 11, in other words, how important are changes in the molar mass of the lower molecular weight species that are preferentially incorporated into the interphase?

5.1. Stationary States vs Equilibria. The general observation at the lower temperatures is a decrease of the interfacial tension with time. Guido et al. investigated the drop size and interfacial tension of the sheared system PDMS/PIB as a function of time. For an isolated small droplet of PIB in PDMS they found a strong increase of σ from 3 to more than 4 mN m^{-1} with a simultaneous reduction of the droplet diameter. For the opposite case (PDMS in PIB) there was no significant change of σ. The third type of experiments they performed with blends containing either 1% or 3% PIB in PDMS into which one small droplet of pure PIB was injected. They found a less pronounced decrease of the drop diameter and after approximately 3 h the droplet size remained constant. To rationalize the fundamentally different findings concerning the influences of time on the interfacial tension of the system PIB/PDMS described in this work and reported in the literature,[4] we must first compare the differences and similarities in the polymer samples used and in the experimental procedures. For this reason, we are comparing the methods in detail. Both analyze the shape of droplets of one phase embedded in the matrix of the other phase, either in the gravitational field or in a shear field. The decisive difference seems to be that we study droplets, which are typically of a diameter between 1.5 and 2 mm (leading to phase volume rations on the order of 30 or more), whereas this dimension is only on the order of 60 μm in the shear experiments. For the kinetic considerations described in section 3.1 this dissimilarity has far reaching consequences, because it signifies that the reservoir for the short chains that are preferentially migrating to the interface is approximately 30 000 times larger in the former case than in the latter case. In other words: The stationary states in shear experiments should last only 3.3×10^{-5} times as long as in the case of pendent drop measurements.

On the basis of the considerations described above, we conclude that the reported augmentation[4] of σ with proceeding time refers to the kinetics of the attainment of *equilibria* during the later state of mass transport from the source phase via interphase into the receiving phase. Because of the minute size of the reservoir in these experiments the *stationary state* can only be upheld for too short a time to be detectable. Under these conditions the concentration x_α of the migrating species in the source phase falls so fast that the first term of eq 2 rapidly becomes too small to keep the flux into the interphase as large as that out of it. For the assessment of the equilibrium information obtained in these experiments, it appears important that it depends on the overall composition of the system as a consequence of the fractionation associated with the partitioning of the different polymer species on the coexisting phases.

The following conclusions concerning the general shape of the time dependence of the interfacial tension can, be drawn from the available data. Immediately after formation of a new interface between two incompatible polymers of broad molecular weight distribution *σ decreases* rapidly because of the preferential incorporation of the shorter chains into the interphase. The effect of this favored migration is slowing down as time proceeds due to some solubility of these lower molecular weight species in the corresponding receiving phases. A steady state is reached, i.e., σ becomes *constant*, as the rates of diffusion into the interphase and out of it become identical (cf. section 3.1). Because of the limited material contained in the source phase and the continuous transport out of the interphase into the interior of the receiving phase this status cannot be upheld indefinitely and the steady state will come to an end. This means that the interfacial tension *increases* with time during that stage as a result of the depletion of the interphase in the short chains leading to low σ values. The just described situation can also be looked at from a more thermodynamic point of view. The steady state should correspond to minimum entropy production achieved by the realization of low σ values. For the minimum in the Gibbs energy, defining the equilibrium state, small interfacial tensions are obvious contributing less than the entropy of mixing associated with the mixing of the receiving phases with the shortest chains of the source phases despite the fact that their concentration will probably remain minute.

Primary data of interfacial tensions as a function of time for the system PDMS 55n/PIB wide within a larger temperature interval corroborate the above interpretation as demonstrated by the following graphs

Part a of Figure 11 gives the results for 30 °C. The time dependence of σ is very similar to that of the blends studied so far. According to the present considerations, this behavior is typical for comparatively high viscosities of the blend components (i.e., low temperatures), where the transport of matter from one phase to the other is rather slow. As the temperature is raised these processes take place much more rapidly. This means that stationary states may already be reached during sample preparation. With the present system, these conditions are realized within the temperature range from 70 to 90 °C; part b of Figure 11 shows the data for 80 °C. Finally, at very high temperature, the transport takes place so rapidly that the stationary states are already over before the measurements start. This is the case with the present blend at temperatures higher than 90 °C as shown in part c of Figure 11 for 110 °C. Under these conditions, the observed time dependence of σ reflects the transport of the short chain components out of the interphase into the receiving phase due to the attainment of the macroscopic thermodynamic equilibrium of the system.

For the system PDMS 87n/PIB wide (higher molar mass of PDMS), the interfacial tensions decrease with time up to approximately 60 °C and become independent of it at the higher temperatures.

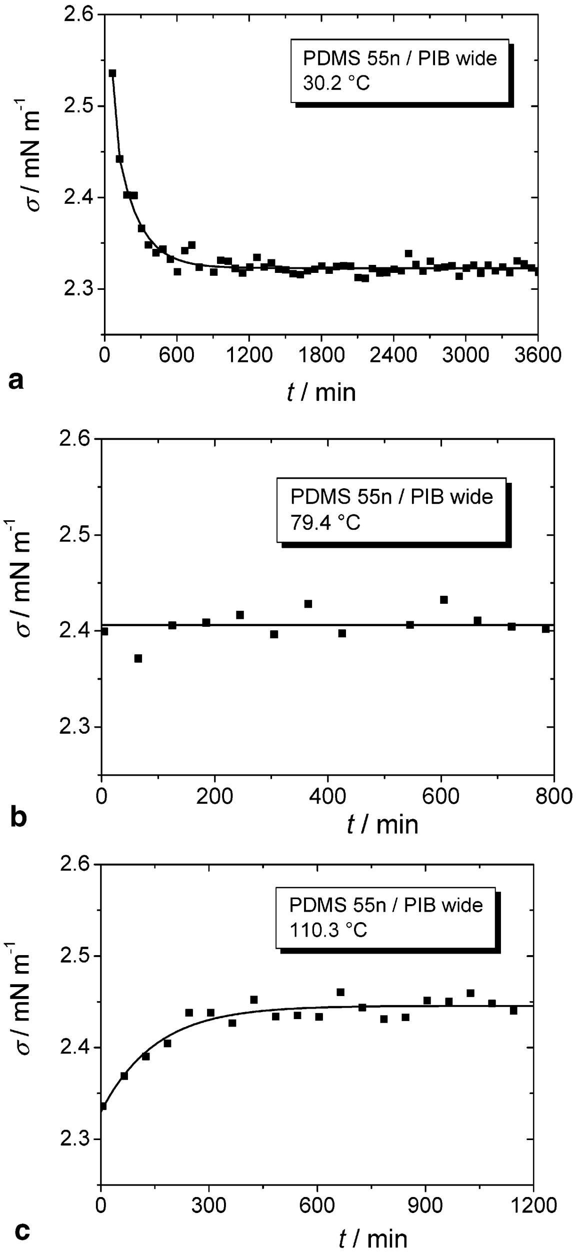

Figure 11. Interfacial tensions as a function of the time at 30, 80, and 110 °C of the system PDMS 55n/PIB wide

Table 3. Activation Energies for the Different Transport Processes and for the Viscous Flow of the Blend Components[a]

α	ω	$E^{\ddagger}_{\tau}$/kJ mol^{-1}	$E^{\ddagger}_{\eta_\alpha}$/kJ mol^{-1}	$E^{\ddagger}_{\eta_\omega}$/kJ mol^{-1}	ϖ_ω
PIB wide	PDMS 87	34.8	59.2	14.2	0.54
PIB narrow	PDMS 87	26.7	54.8	14.2	0.69
PIB wide	PDMS 55	45.6	59.2	14.6	0.30
PDMS 87	PIB wide	49.0	14.2	59.2	0.77
PDMS 87	PIB narrow	49.3	14.2	54.8	0.86
PDMS 55	PIB wide	65.9	14.6	59.2	≈1

[a] The parameter ϖ_ω is calculated by means of eq 19. For the system PDMS 55/ PIB narrow the activation energy $E^{\ddagger}_{\tau}$ is larger than $E\omega^{\ddagger}_{\eta}$ and one would consequently obtain $\varpi_\omega > 1$; taking the experimental errors for the different $E^{\ddagger}$ values (±10%) into consideration, it appears justified to set $\varpi_\omega \approx 1$.

5.2. Activation Energies. Equations 11 and 20 testify to a complicated interrelation between the temperature dependence of τ and that of η_α and η_ω. In case the assumptions underlying the current consideration hold true, $E^{\ddagger}_{\tau}$ should generally lie somewhere between $E^{\ddagger}_{\eta_\alpha}$ and $E^{\ddagger}_{\eta_\omega}$. The evaluation of the data presented in the last section according to the above relation corroborates this conclusion as demonstrated in Table 3. According to eq 20 the exact value of ϖ_α does not only depend on the η values and their temperature dependence, but also on the kinetic constants k_1^* and k_2^*. To gain first information on the contributions of these constants we assume on a trial basis that they are identical. The ϖ_α values calculated in this manner lead to the conclusion that $k_1^* \gg k_2^*$ for the transport of PIB wide or PIB narrow into PDMS 87, whereas these constants are comparable for the transport of PDMS 87 into PIB wide or PIB narrow.

5.3. The Exponent *d*. The analysis of the experimental data on the diffusion of PDMS 87 and PDMS 55 into PIB wide according to eq 24 leads to d values rising from 3.3 at 30 °C to 5.1 at 60 °C, where the average for all measurements amounts to 4.0. The information on the diffusion of PIB narrow (index I) and PIB wide (index II) into PDMS 87 in combination with the modeled polydispersities ($f_{\min\ \mathrm{II}} = 2.87$ and $f_{\min\ \mathrm{I}} = 2.19$) yields exponents which increase from 2.9 at the lowest temperature up to 3.9 for the highest temperature, with an average of 3.0. The average of all eight measurements leads to $d = 3.5$.

The order of magnitude of the estimated influences of the chain length of the migrating species appears reasonable, particularly in view of the various simplifying assumptions and considerable experimental errors (in particular with ϖ_ω). In any case it testifies that the influences of chain length dominate that of the viscosity by far. In view of the just described uncertainties, an interpretation of the observed systematic changes of d with temperature must presently remain open. For the same reason, an discussion whether there exists an interrelation between the exponent d of eq 7 and the exponent z of eq 1 must be postponed.

6. Conclusions

The present results in combination with published data document that the polydispersities of the blend components play an important role for the time evolution of the interfacial tension. The reason for this performance lies in the fact that the preferential incorporation of the lower molecular weight species into the interphase reduces σ. The early stages of $\sigma(t)$ are characterized by the migration of the shorter chain components from the source phase into the interphase and the corresponding diminution of the interfacial tension. This process slows down to the extent that the reservoir is emptied and the interfacially active molecules are transported from the interphase into the receiving phase. A stationary state is reached once the flows into the interphase and out of it become equal. This particular situation comes to an end as soon as the required influx can no longer be upheld. From now on, σ increases with time because the transport into receiving phase continues and the concentration of the short chains in the interphase falls. It is evident that the just described features must be kept in mind if one compares information on interfacial tension stemming from different experimental methods.

For the processes taking place immediately after the formation of a new interface between incompatible polymers, we have established a kinetic model. A detailed analysis of the corresponding characteristic times in the absence and in the presence of a compatibilizer reveals the central role of the chain lengths of the migrating lower molecular fraction of the different polymers and of the bulk viscosities of the coexisting phases.

By the variation of the *average* chain length of PDMS (comparable polydispersity) and second by the variation of polydispersity PIB (equal M_n), we found that the influence of the molecular weight of the migrating species depends with power of around 3.5 and is therefore much more pronounced than the influence of the viscosity (power of 1). According to the kinetic model established for the time evolution of the interfacial tension, the viscosities of the blend components contribute only linearly to the different characteristic times, but in a complex manner. For the assessment of temperature influences on the transport processes an interrelation between the their activation energies and the activation energies for η_α and η_ω following from this model proves very helpful. The postulated relation is well corroborated by the experimental findings.

Measurements with the ternary systems affirm the expected considerably slower transport of the compatibilizer into the interface as compared with that of the low molecular weight fractions of the homopolymers. Moreover, they demonstrate that the presence of the block copolymer leads to a pronounced slowing down of the diffusion of the low molecular weight species of the homopolymers contained in this phase. This observation is attributed to thermodynamic and hydrodynamic interactions between the homopolymer and the corresponding block of the copolymer additive.

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Supporting Information Available: Table 4, giving the characteristic times and fit parameters according to eq 13 at different temperatures for the blends PDMS 87n/PIB $_{\text{wide}}$, PDMS 87n/PIB $_{\text{narrow}}$, and PDMS 55n/PIB $_{\text{wide}}$, and Table 5, giving the same parameters for the ternary blend PDMS 87n/(PIB $_{\text{wide}}$ + 0.03 wt % CoPo). This material is available free of change via the Internet at http://pubs.acs.org.

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