Ellipsometric Measurements of Positive χ Parameters between Dissimilar Polymers and Their Temperature Dependence

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ABSTRACT: The interfacial thickness between immiscible polymers, polystyrene/polymethylmethacrylate (PS/PMMA) and PMMA/random copolymers of styrene and acrylonitrile (PMMA/SAN), was obtained by ellipsometry in the temperature range from 140 to 170 °C. Using these values, it is possible to calculate the polymer–polymer interaction parameter χ_{AB} as well as the segmental interaction parameters $\chi_{i/j}$. It has been shown that all three segmental interaction parameters of the system PMMA/SAN, i.e. $\chi_{S/MMA}$, $\chi_{AN/MMA}$, and $\chi_{S/AN}$, are decreasing with increasing temperature, but the polymer–polymer interaction parameters between PMMA and SAN in a certain copolymer composition range are increasing with temperature, leading to LCST (lower critical solution temperature) behavior. It has to be considered that the temperature dependence of segmental interaction parameters is governed by changes of interactions as well as free volume contributions, but in copolymer blends it raises the possibility of LCST behavior which is not driven by the free volume term. The experiments predict UCST (upper critical solution temperature) behavior in blends of low molecular weight PMMA and PS, which is in agreement with experimental findings. Furthermore, segmental interaction parameters and their temperature dependence for blends of random copolymers of styrene and methylmethacrylate (SMMA) and poly(vinyl methyl ether) (PVME) were estimated. The segmental interaction parameter $\chi_{S/VME}$ is increasing with increasing temperature, implying a free volume contribution to the well-known LCST behavior.

Introduction

Ellipsometry is a powerful tool for measuring the interfacial thickness in polymer blends. These measurements can be carried out for immiscible as well as miscible polymer blends. For miscible blends the investigation of changes of the interfacial thickness with time at a fixed temperature makes it possible to calculate mutual diffusion coefficients.[1] In this paper we want to focus on immiscible polymer blends. Here, the interfacial layer can be studied in an equilibrium state. By use of the theory of Helfand et al.,[2,3] the interaction parameter χ can be deduced from measurements of the interfacial thickness. Thus it provides one of the rare opportunities to study positive χ parameters for immiscible blends. The method is relatively easy to handle and does not need deuterated samples as, e.g., required for neutron-scattering experiments. Therefore, one can obtain positive χ parameters and their temperature dependence on a routine basis. The limitations of ellipsometry are given by refractive index differences which should be greater than approximately 0.02. The error of the method becomes tremendous when the system has a small refractive index difference and a thin interface (equivalent to a large positive χ parameter). Therefore, copolymer blends showing a miscibility gap are very suitable for ellipsometric studies. Because of a large number of available copolymer pairs, one can easily find systems with relatively large refractive index differences, and when copolymer compositions just outside the miscibility gap are chosen, the χ parameter can be set to be positive but very small, leading to a thick interface. In this paper we deal mainly with the system polymethylmethacrylate/poly(styrene-*ran*-acrylonitrile) (PMMA/SAN). This system is suitable because it shows a miscibility window dependent on copolymer composition and temperature.[4–6] On the basis of these results, we will extend the discussion on the temperature dependence of segmental interaction parameters in blends of poly(vinyl methyl ether) (PVME) with random copolymers of styrene and methylmethacrylate (SMMA).

Experimental Section

The polymers used in this study are listed in Table I. The bilayer specimen was prepared by mounting a thin film of SAN (~0.5 μm) on the surface of a thick PMMA substrate (~0.5 mm) as follows. PMMA was melt-pressed between two silicon wafers in order to obtain an optical flat surface. PS and SAN-5.7 were dissolved in monochlorobenzene, and SAN-38.7 was dissolved in cyclohexanone. The code SAN-x means wt % acrylonitrile in SAN. The 6 wt % solutions of polystyrene and SAN, respectively, were filtered through a 0.22-μm Millipore membrane to remove dust particles. Films with a uniform thickness were prepared by spin-coating of the solution on a silicon wafer. Then the film was floated off onto the water surface and picked up with the PMMA substrate. Finally, the bilayer specimen was dried in a vacuum oven at 60 °C for 24 h. Ellipsometric measurements were carried out using an autoellipsometer EL-8, Optec Co. Ltd. The wavelength of the laser was 632.8 nm, and the incident light beam had an angle of 70° to the bilayer specimen. The bilayer specimen was brought into a heating cell under nitrogen, and the temperature during isothermal runs was kept ±0.1 °C. The measurents were limited from 140 to 170 °C. Below 140 °C it should take a very long time to reach the equilibrium state, caused by glass transition effects. Above 190 °C the interfacial thickness during the measurement is continuously increasing, suggesting that thermal degradation of PMMA takes place. The calculations are based on a four-layer model, air–SAN–interface–PMMA. Here, the refractive indices of neat SAN and PMMA films were measured by ellipsometry. The refractive index of air was taken as 1, and the refractive index of the interfacial layer was assumed to be the mean value between SAN and PMMA. For these calculations a stepwise approximation of the refractive index has to be assumed. This generates a somewhat thicker interface than a wedge-shaped fit of the tanh concentration gradient profile. Therefore, a correction factor was introduced.[7] For detail of calculations see also ref 8.

Background: Phase Behavior of PMMA/SAN

For the blend system PMMA/SAN three sets of segmental interaction parameters $\chi_{i/j}$ are known from the literature[4–6] and listed in Table II together with the values

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Table I
Molecular Weight Data for the Polymers

sample	source	M_w	M_w/M_n
PMMA	Sumitomo GI-633	151 000	2.1
PS	Denka-Styrol GP-1	180 000	2.0
SAN-5.7[a]	Mitsubishi Monsanto	259 000	2.2
SAN-38.7[a]	Mitsubishi Monsanto	74 000	2.2

[a] Number means wt % acrylonitrile in SAN.

Table II
Binary Interaction Parameters Obtained by Ellipsometric Measurements and from Literature[a]

temp/°C	$\chi_{S/MMA}$	$\chi_{AN/MMA}$	$\chi_{S/AN}$
130	0.03[c]	0.6954	1.404
b	0.03[c]	0.46	0.83
140	0.0529	0.357	0.875
150	0.0529	0.357	0.875
160	0.0262	0.172	0.417
170	0.00925	0.0525	0.123
180	0.01	0.05	0.12

[a] The values at 130 °C are taken from Nishimoto et al.[5] and the values at 180 °C are from Kammer et al.[4] [b] Values obtained by Cowie et al.,[6] no temperature given. [c] This value obtained by light scattering[10] was used in order to obtain the other segmental interaction parameter.

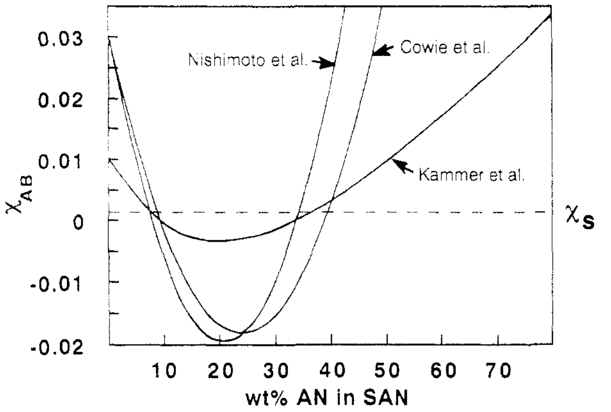

Figure 1. χ_{AB} parameter dependence on the copolymer composition, calculated by using the $\chi_{i/j}$ parameters listed in Table II and taken from refs 4–6.

obtained from ellipsometric measurements which will be discussed below. The interaction parameter between PMMA(A) and SAN(B) is then given by[9]

$$\chi_{AB} = \beta\chi_{S/MMA} + (1-\beta)\chi_{AN/MMA} - \beta(1-\beta)\chi_{S/AN} \quad (1)$$

β means mole fraction of styrene in SAN. It should be noted that different authors are using different definitions of β and obtain different χ parameters, which of course can easily be converted. The parameters χ_{AB} dependent on the copolymer composition calculated by using the three sets of segmental interaction parameters are shown in Figure 1. The apparent discrepancy between the three curves arises from the different methods used for the calculation of $\chi_{i/j}$. These different methods refer to different temperatures, and thus it must be taken into consideration that χ_{AB} and $\chi_{i/j}$ are functions of the temperature. The values of Kammer et al.[4] were obtained from critical data of light-scattering measurements at about 180 °C using a copolymer composition in mole fractions. Cowie et al.[6] fitted the $\chi_{i/j}$ parameter to the miscibility area with dependence on the copolymer composition β taken as the weight fraction. Nishimoto et al.[5] fitted their data at 130 °C using volume fractions. Cowie et al. as well as Nishimoto et al. took one temperature and the two border values of β in the miscibility window, where χ_{AB} equals to χ_s, and thus the χ parameter at the spinodal is given by

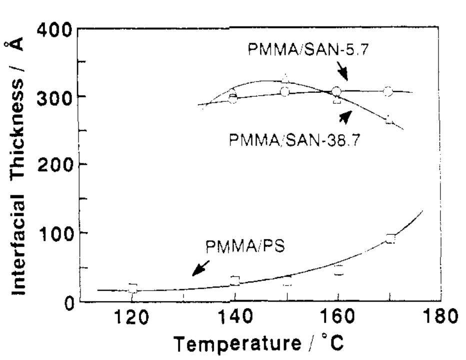

Figure 2. Temperature dependence of the interfacial thickness. The value at 120 °C was obtained by neutron reflection measurements and was taken from the literature.[11] For error discussion see ref 21.

$$\chi_s = \frac{1}{2}\left(\frac{1}{\phi_A r_A} + \frac{1}{\phi_B r_B}\right) \quad (2)$$

where ϕ_i is the volume fraction and r_i the number of segments. At this point it should be noticed that it seems to be better to take the stability limit of the homogeneous region of the blend systems under investigation as $\chi_{AB} < \chi_s$ rather than $\chi_{AB} < \chi_c$, the χ parameter at the critical point. This difference, even if it is only very small, should be considered because the miscibility windows under discussion are designed with dependence on copolymer composition and temperature for a fixed blend ratio. But this blend ratio might be faraway from the critical point. Replacing χ_{AB} by χ_s in eq 1 gives just two equations but three unknown parameters. Thus Nishimoto et al.[5] as well as Cowie et al.[6] used $\chi_{S/MMA} = 0.03$ obtained from light-scattering data under quasi optical Θ conditions in ternary solutions at room temperature.[10] This procedure neglects the temperature dependence of $\chi_{S/MMA}$ and might lead to different values. In the following we want to discuss the $\chi_{i/j}$ parameters and their temperature dependence obtained from ellipsometric measurements and compare these data with values discussed above.

Results and Discussion

Figure 2 shows the interfacial thickness dependent on the temperature for blends of PMMA/PS, PMMA/SAN-5.7, and PMMA/SAN-38.7. The value of the interfacial thickness at 120 °C was obtained by neutron reflection measurements.[11,12] As can be seen, the interfacial thickness of the PS/PMMA blend increases with temperature. Also the interfacial thickness of PMMA/SAN-5.7 increases slightly whereas the interfacial thickness of the system PMMA/SAN-38.7 decreases slightly in the temperature range from 140 to 170 °C. According to the recent theory the interfacial thickness λ is connected with the interaction parameter χ_{AB} by[3]

$$\lambda = \frac{2b}{(6\chi_{AB})^{1/2}}\left[1 + \frac{\ln 2}{\chi_{AB}}\left(\frac{1}{r_A} + \frac{1}{r_B}\right)\right] \quad (3)$$

where r_i is the number of segments and b is the Kuhn segment length (8 Å). Thus it is possible to convert the interfacial thicknesses into the χ_{AB} parameter, as depicted in Figure 3. The interaction parameter between PS and PMMA decreases with increasing temperature. Both interaction parameters between SAN-5.7 and PMMA as well as SAN-38.7 and PMMA show only a very weak temperature dependence. Taking these data, it is possible to calculate the two unknown segmental interaction

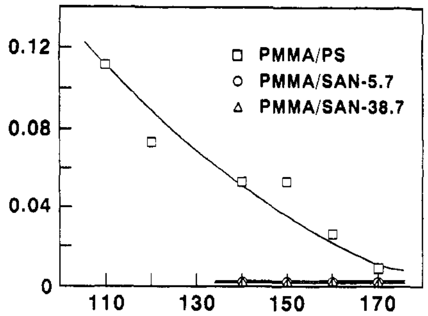

Figure 3. Temperature dependence of χ_{AB} parameters calculated by using eq 3. The value of the PMMA/PS blends at 110 °C was calculated from the phase behavior of low molecular weight compounds (see text).

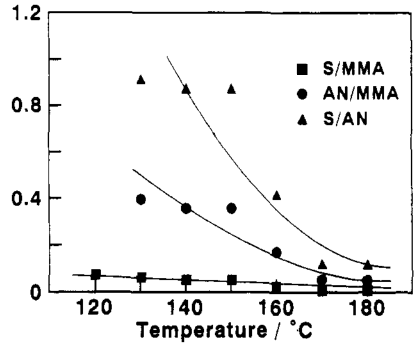

Figure 4. Dependence of the segmental interaction parameters $\chi_{i/j}$ of the PMMA/SAN system on the temperature. The values at 130 °C are recalculated from ref 5 (see text) and at 180 °C from ref 4. The lines are least squares fits.

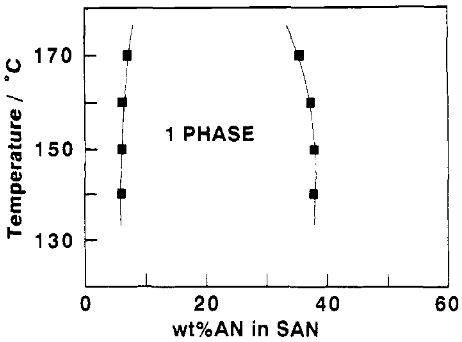

Figure 5. Miscibility window of PMMA/SAN blends calculated from the segmental interaction parameter in the temperature range from 140 to 170 °C.

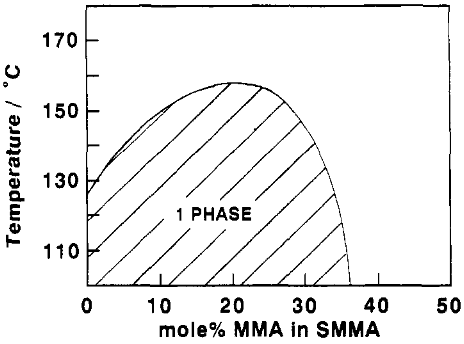

Figure 6. Miscibility gap for 50/50 PVME/SMMA blends are taken from ref 14.

parameters. In eq 1 the interaction parameter χ_{AB} and the segmental interaction parameter $\chi_{S/MMA}$ are known for various temperatures. Furthermore, there are for every temperature two different copolymer compositions β (10.6 and 55.3 mol % acrylonitrile in SAN) which can be used in eq 1. Thus there are two unknown parameters and two equations for every temperature under investigation. Figure 4 shows the calculated segmental interaction parameters $\chi_{AN/MMA}$ and $\chi_{S/AN}$ as well as the experimentally determined parameter $\chi_{S/MMA}$ with dependence on the temperature. Additionally, Figure 4 contains the segmental interaction parameter given by Kammer et al.[4] at 180 °C and the values of Nishimoto et al.[5] at 130 °C recalculated by inserting the border values of β of their miscibility window at 130 °C and the $\chi_{S/MMA}$ parameter obtained from interfacial thickness data (about 0.064) into eq 1. As can be seen, there is a fairly good agreement between all data. The segmental interaction parameters become smaller with increasing temperature. The values of $\chi_{AN/MMA}$ and $\chi_{S/AN}$ are at 170 °C well above χ_s. That means the blends of PAN and PMMA as well as PAN and PS are always in the two-phase region at the temperatures under discussion. In Figure 4 it can also be seen that the segmental interaction parameter $\chi_{S/MMA}$ approaches nearly the value of χ_s, suggesting the possibility of UCST behavior of PS/PMMA blends, at least for low molecular weight compounds. This suggestion is proved by experimental findings showing that a 50/50 blend of PS of M_w = 1000 and PMMA of M_w = 12 000 shows UCST behavior at 110 °C.[13] Thus at 110 °C the $\chi_{S/MMA}$ parameter is equal to χ_s (=0.112). This value fits well to our data shown in Figure 4. As shown, all three segmental interaction parameters are decreasing with increasing temperature. This seems apparently not to be in agreement with the fact that the PMMA/SAN blends display LCST behavior. Because of the structure of eq 1, which weights the segmental interaction parameter differently, it is possible that χ_{AB} increases with temperature, resulting in LCST behavior. Taking the values from interfacial thickness measurements, one can calculate the data for the miscibility window of PMMA/SAN and compare with literature data.[5,6,18] The data shown in Figure 5 are in good agreement with cloud point measurements.

Having the temperature dependence of the parameter $\chi_{S/MMA}$, it is possible to extend the analysis for different systems. For instance, it has been known that random copolymers of styrene and methylmethacrylate (SMMA) show a miscibility gap with poly(vinyl methyl ether) (PVME).[14,15] This is shown in Figure 6. A 0% methylmethacrylate content in the random copolymer represents the blend of PS with PVME. Blends of PS with PVME show LCST behavior dependent on the molecular weights. Replacing PS by SMMA with an increasing amount of methylmethacrylate changes the miscibility behavior and finally leads to complete immiscibility. Miscibility of the SMMA/PVME system occurs inside the line of Figure 6. Taking the temperature dependence of the $\chi_{S/MMA}$ parameter and the border values of β in the miscibility window, it is again possible to calculate the parameters $\chi_{MMA/VME}$ and $\chi_{S/VME}$. The result is shown in Figure 7. As expected, the $\chi_{S/VME}$ parameter increases with increasing temperature, suggesting a free volume contribution. This is in agreement with the occurrence of LCST behavior in the temperature range under discussion. With this set of $\chi_{i/j}$ parameters dependent on the temperature, it is again possible to fit the miscibility area with dependence on temperature and copolymer composition.

Concluding Remarks

Thus it has been shown that the phase behavior of blends containing a random copolymer can be explained by taking into consideration the temperature dependence of the segmental interaction parameters $\chi_{i/j}$. This was also done recently by Cimmino et al. in a different way for blends

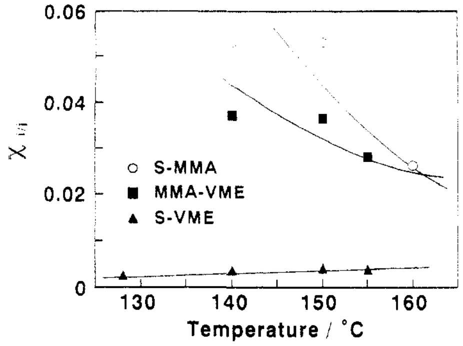

Figure 7. Dependence of the $\chi_{i/j}$ parameters of the system PVME/SMMA on the temperature.

of PPO and poly(*o*-chlorostyrene-*ran*-*p*-chlorostyrene).[16] Most surprisingly in the blend system PMMA/SAN is the fact that all three segmental interaction parameters are decreasing with increasing temperature but the χ parameter between PMMA and SAN for certain copolymer compositions increases with temperature resulting in LCST behavior which is in agreement with experimental findings.[18] This fact leads to a number of general questions. It has been figured out that the general behavior in polymer blends is LCST rather than UCST behavior. But it should be recognized that the overwhelming number of systems displaying LCST behavior comprise at least one random copolymer. It has generally been accepted that the temperature dependence of the χ parameter is governed by two effects; the interaction term leading to smaller χ values with increasing temperature in the case where there are no specific interactions, i.e. positive χ parameters, and the free volume term leading to higher χ values with increasing temperature.[17] Thus the interaction term would favor UCST behavior and the free volume term LCST behavior. According to a mean-field theory, the parameter χ_{AB}, which is responsible for the phase behavior in random copolymer/homopolymer blends, is a function of copolymer composition and three segmental interaction parameters (cf. eq 1). These parameters again may contain interaction and free volume terms. Thus the situation in copolymer blends is very complex. Theoretically, the possibility exists that the different temperature dependences of the contributions of interactions to the segmental interaction parameters $\chi_{i/j}$ may lead to LCST behavior without any obvious influence of free volume changes. Patterson et al.[19] predicted that the free volume term in polymer blends might be frequently of minor influence, because of the smaller number of the external degrees of freedom the expansion coefficients of polymers are always very similar, compared with solvent/solvent or solvent/polymer systems. The free volume difference between two polymers can generally be characterized by the parameter τ:[19]

$$\tau = 1 - \frac{T_A^*}{T_B^*} \tag{4}$$

where T_A^* and T_B^* are reference temperatures of the neat components and can be obtained, e.g., by the Flory equation-of-state theory[20] and appropriate thermal expansion coefficients. Patterson et al.[19] give a τ value for blends of PMMA and PS of approximately 0. Using this value, they predict an exponential decay of $\chi_{S/MMA}$ with temperature and UCST behavior for low molecular weight blends. This is in excellent agreement with our results. In contrast the τ value of blends of PS and PVME is given to be larger (approximately 0.12) and thus the calculations show that the possibility of LCST behavior arises from the free volume term.[19] Furthermore, when suitable sets of temperature-dependent χ parameters are chosen the explanation for the simultaneous occurrence of LCST and UCST behavior can easily be given. Also here it should be realized that the majority of systems displaying both LCST and UCST behavior contain a random copolymer. But to have a better understanding of the general behavior of random copolymer blends, it should be necessary to obtain complete sets of P–V–T data.

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(21) Every point is the average of several measurements carried out after the interfacial thickness reached a constant value with dependence on time.[8] We estimated the average error to be ±10 Å. This generates a negligible error of the χ values for thick interfaces, as e.g. in PMMA/SAN-5.7 and PMMA/SAN-38.7 blends. It becomes only influencial for thin interfaces. At 170 °C $\chi_{S/MMA}$ is 0.0093 and the fluctuation would be in the range from 0.011 to 0.009. Very strong fluctuations exist only for $\chi_{S/MMA}$ at 150 and 140 °C; e.g. at 140 °C $\chi_{S/MMA}$ is 0.05 and the maximum value would be 0.113 and the minimum value 0.032. But the tendency of $\chi_{S/MMA}$ was proved by two independent methods: neutron reflection measurements (error ±5 Å[11]) and cloud point measurements. Thus for the fitted curves and the general temperature dependence of χ parameters the error is within reasonable limits.

Registry No. PMMA (homopolymer), 9011-14-7; PS (homopolymer), 9003-53-6; SAN (copolymer), 9003-54-7; PVME (homopolymer), 9003-09-2; SMMA (copolymer), 25034-86-0.