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COMPATIBILITY OF A STATISTICAL COPOLYMER P(EMA-CO-MMA) WITH PS AND PMMA

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Summary: The compositions of coexisting phases and the interface widths in blends of a statistical copolymer of poly(ethylmethacrylate - co - methylmethacrylate) (P(EMA_{1-x}-co-MMA_x)) and a deuterated polystyrene (PS(D)) as well as a deuterated poly(methylmethacrylate) (PMMA(D)) have been investigated by neutron reflectometry (NR). Interaction parameters are calculated from the compositions of coexisting phases and the interface width values. Utilizing a novel two dimensional scheme for graphical representation of the interaction parameters, the results are in very good agreement with studies on the interaction parameters for PS/PMMA, PS/PEMA and PEMA/PMMA blends. In particular, $\chi_{EMA/MMA}$ deduced from a NR experiment on a P(EMA-block-MMA(D)) diblock copolymer fits excellent into the scheme.

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Introduction

Controlling the compatibility between different polymers is one of the major problems in the field of polymers. Many efforts have been expended to optimize polymer blends to design materials with properties tailored to specific uses. Due to the chain structure of polymers, the entropy of mixing is largely reduced compared to simple liquids, and thus, most polymer pairs are incompatible1).The technique of neutron reflectometry (NR) enables the investigation of incompatible polymer blends1). NR has a good sensitivity for the interface width in a range typically smaller than 15 $nm^{2)}$. The equilibrium interface width between incompatible polymers is typically in the range between 2 and 15 nm, depending on the compatibility of the components. During Annealing above the glass transition temperatures the interface width increases with time, reaching an equilibrium value, which according to mean - field theory is determined by the Flory - Huggins - Stavermann interaction parameter χ1). The quantity χ is a measure of polymer compatibility, although it is not well understood on a molecular basis and is often used as an empirical parameter. However, this parameter allows a quite detailed description of thermodynamics of phase separation for any given polymer pair within mean field theory 3-6). We have demonstrated that both the interaction parameter χ and the segment length b can be determined for incompatible polymer blends utilizing NR7). The molecular weight dependence of the interface width between poly(methylmethacrylate) (PMMA) and deuterated polystyrene (PS(D)) was analysed and $\chi = 0.0326$ and $b = 0.73$ nm were deduced from the data. Thus, NR can be regarded as a continuation of small - angle neutron scattering (SANS) into the two - phase region in order to achieve a more comprehensive understanding of polymer miscibility8). We have investigated earlier also incompatible binary blends consisting of PS(D) and various poly(alkylmethacrylates) (PAlkylMA)9). A scheme for predicting compatibility of the PAlkylMA with PS and PMMA was formulated introducing a graphical representation of interaction parameters. In that scheme distances mirror the respective square root of the interaction parameters between particular polymer pairs.

The scheme represents also interaction parameters between statistical copolymers10). It is the purpose of this article to focus on the interaction parameters of the three polymers PS, PMMA and polyethylmethacrylate (PEMA). In particular, the interactions between a statistical copolymer P(EMA_{1-x}-co-MMA_x) and a deuterated PS(D) as well as a deuterated PMMA(D) are under consideration.

Theory

Interfaces between incompatible polymers

The interface width a_I between incompatible polymers is controlled by the Flory -Huggins - Stavermann (FHS) interaction parameter χ [1,6,11,12,13]. For chains of infinite molecular weight the interface width is given by [1,6,11,12,13]

$$a_I = \frac{2b}{\sqrt{6\chi}} \tag{1}$$

where b is the characteristic segment length. The corresponding volume fraction profile can be calculated with a mean - field description[1,6,11,12,13]

$$\phi(z) = \frac{1}{2}\left(1 + \tanh\frac{2z}{a_I}\right) \tag{2}$$

z is the coordinate normal to the interface. Taking into account finite chain length N_1 and N_2, Broseta et al.[13] derived

$$a_I = \frac{2b}{\sqrt{6\left(\chi - 2\ln 2\left(\frac{1}{N_1} + \frac{1}{N_2}\right)\right)}} \tag{3}$$

For the interface between two incompatible polymers with slightly different segment lengths b_1 and b_2 one can use an effective segment length b in Eqs. (1) and (3) [11]

$$b^2 = \frac{b_1^2 + b_2^2}{2} \tag{4}$$

Interaction parameter in statistical copolymer blends

Within the mean - field theory the interaction parameter between two different statistical copolymers $P(A_xB_{1-x})$ and $P(C_yD_{1-y})$ depends in a parabolic way on the copolymer compositions x and y [14]:

$$\begin{aligned}\chi = {} & (1-x)(1-y)\chi_{A/C} + (1-x)y\chi_{A/D} + x(1-y)\chi_{B/C} + xy\chi_{B/D} \\ & - x(1-x)\chi_{A/B} - y(1-y)\chi_{D/C}\end{aligned} \tag{5}$$

The relevant prefactors of the parabolic dependency are given by 6, in general, different pair interaction parameters between the corresponding pure components, χ_{AB}, χ_{AC}, χ_{AD}, χ_{BC}, χ_{BD} and χ_{CD}. For the case of a homopolymer P(C) and a statistical copolymer $P(A_xB_{1-x})$ Eq. (5) simplifies (y = 0) to

$$\chi = s^2 = x\chi_{B/C} + (1-x)\chi_{A/C} - x(1-x)\chi_{A/B} \qquad (6)$$

A novel scheme for the graphical representation of the last equation has been suggested and is shown in Fig. 1.$^{10)}$. Distances mirror direct the square roots of interaction parameters.
In particular, the distance s represents the square root of the interaction parameter given by Eq. (6).

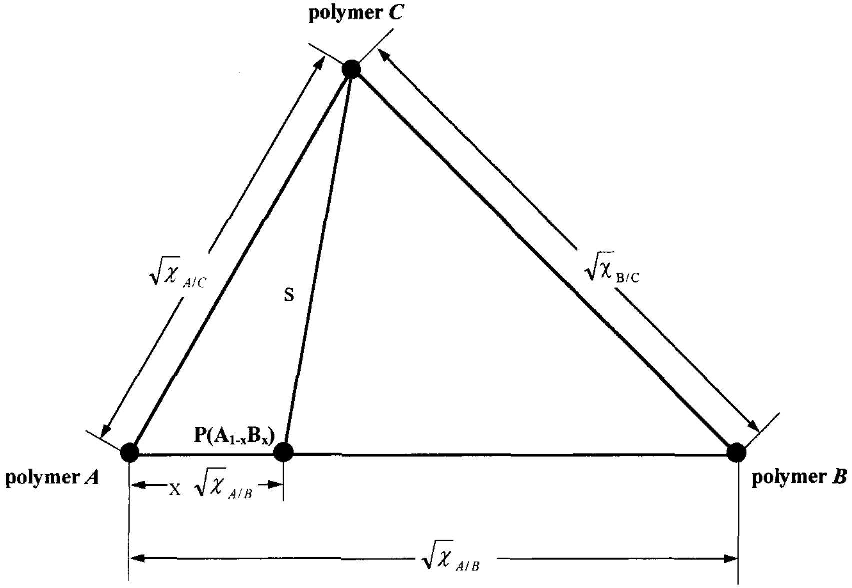

Fig. 1: Two - dimensional scheme representing square root of the interaction parameter between a homopolymer C and a statistical copolymer $P(A_{1-x}B_x)$ by the distance s.

Experiment

In order to understand the interactions of a $P(EMA_{1-x}\text{-co-}MMA_x)$ and a deuterated polystyrene (PS(D)) as well as a deuterated poly(methylmethacrylate) (PMMA(D)), two bilayer samples were prepared. The deuterated material were prepared as the top layer respectively. The molecular characteristics of the polymers used are given in Table 1.

Polymer	PS(D)	PMMA(D)	P(EMA$_{1-x}$-co-MMA$_x$)
M_w (kg/mol)	676	160	57
M_w/M_n	1.05	1.06	1.18
Tg (°C)	104	125	87

Table 1. Molecular characteristics of the polymers used. M_w and M_n represent the weight and number - average molecular weight, respectively. T_g is the glass transition temperature.

The molecular weight is obtained by gel permeation chromatography (GPC). Glass transition temperatures are taken as an average from heating and cooling runs at 10K/min in differential scanning calorimetric measurements. The composition x = 0.28 of the statistical copolymer P(EMA$_{1-x}$-co-MMA$_x$) was determined by ^{1}H NMR.

Materials were dissolved in toluene at a concentration of about 15 g/l and then deposited by spin coating15) onto float glass plates (10 x 10 cm^2). This method provides very smooth films with thicknesses of about 100 nm. Subsequently, bilayer samples were prepared using the deuterated PS(D) or PMMA(D) as the top layer and P(EMA$_{1-x}$-co-MMA$_x$) as the respective bottom layer. The detailed procedure of the bilayer preparation is described elsewhere11). The NR experiments were performed at TOREMA II at GKSS Research Centre, Geesthacht, Germany, with the wavelength λ fixed at 0.43 nm. The angle of incidence θ of the neutrons at the sample was varied in the range between 0.1° and 1.5°. Analyzing the specular reflectivity2) yields information on the neutron refractive index and composition profile. The refractive index profile is assumed to vary only in the direction z perpendicular to the interfaces. Error functions characterized by their variances σ_1 and σ_2, respectively, are employed to describe the roughnesses of the interfaces air / top-material and bottom-material / substrate (see Figure 2). A refractive index profile according to Eq. (2) with the characteristic parameter a_I is used for the polymer / polymer interface. The resulting refractive index profile can be approximated by a sequence of thin homogenous layers and reflectivities of such a multilayer can be calculated2,16). Neglecting absorption, the refractive index for neutrons travelling in a medium is given by 2)

$$n = 1 - \frac{\lambda^2}{2\pi} N_A \sum_i \frac{\rho_i b_i}{A_i} \tag{7a}$$

where N_A is Avogadro's number, ρ_i the density, b_i the scattering length (listed in the literature[17]) and A_i the atomic weight of species i. For the case of polymers, Eq. (7a) can be rewritten as

$$n = 1 - \frac{\lambda^2}{2\pi}\frac{N_A\rho}{M}\sum_{repeat\ unit} b_i \tag{7b}$$

The sum runs over the atoms in the repeat unit and M is the molecular weight of the repeat unit (monomer); ρ is the mass density of the polymer.

The measured reflectivity is a function of the normal component of the wave vector k_z given by

$$k_z = \frac{2\pi}{\lambda}\sin\theta \tag{8}$$

and thus of the angle of incidence θ and the wavelength λ.

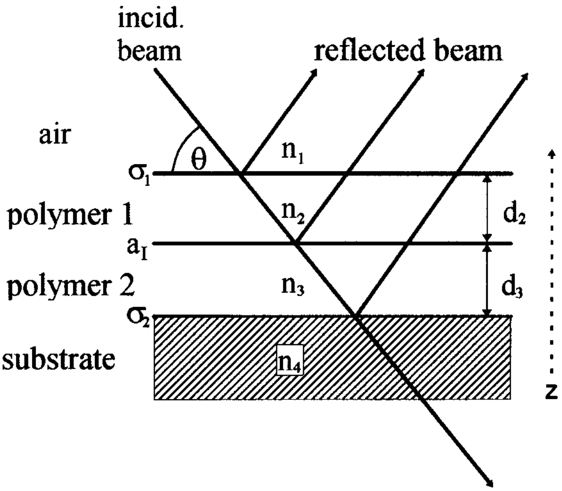

Fig. 2. Schematic diagram of a neutron reflection experiment from a bilayer sample. Parameters are explained in the text.

Minimizing the deviation between experimental and calculated reflection curves yields interfacial profiles and thickness of the individual layers with an accuracy of up to 0.1 nm. Performing measurements of the samples as prepared and after annealing, the initial roughness a_{I0} and the equilibrium value a_{Ie} can be obtained, respectively. One verifies in additional experiments that the equilibrium is reached at a specific temperature by performing the same experiment after several annealing times and seeing that the reflectivity curve remains unchanged. NR experiments are performed at room temperature after annealing and quenching. To determine the interfacial width a_I the initial roughness is taken into account by the following equation 7,11,18)

$$a_I = \sqrt{a_{Ie}^2 - a_{I0}^2} \tag{9}$$

Results and Discussion

As a typical example for a NR investigation concerning the interface between strong incompatible polymers, the reflection curves and corresponding refractive index profile before and after annealing of the PMMA(D) / P(EMA_{1-x}-co-MMA_x) bilayer are shown in Figures 3 and 4, respectively.

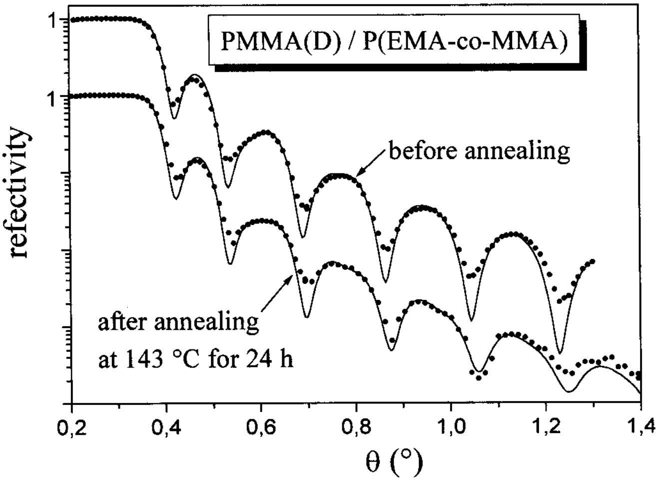

Fig. 3: Neutron reflectivity data (•) and fits (solid curves) before and after annealing of the PMMA(D) / P(EMA_{1-x}-co-MMA_x) bilayer sample. For better clearness, the upper curves are shifted vertical by a factor 10 on the logarithmic reflectivity scale.

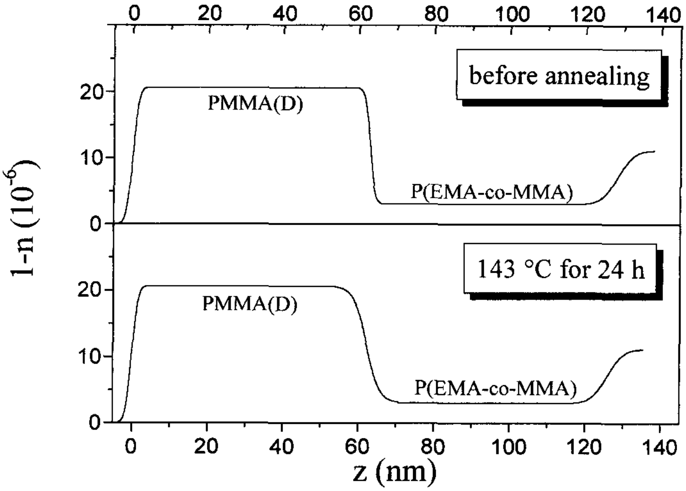

Fig. 4: Neutron refractive index profile (1-n) of the PMMA(D) / P(EMA$_{1-x}$-co-MMA$_x$) bilayer before and after annealing. Shown curves correspond to best fits of calculated reflection curves shown in Fig. 3.

The study on the PS(D) / P(EMA$_{1-x}$-co-MMA$_x$) bilayer represents a moderately incompatible polymer blend. The reflection curve (see Figure 5) before annealing has the same features as the reflection curve of the the PMMA(D) / P(EMA$_{1-x}$-co-MMA$_x$) bilayer before annealing (Figure 3). However, the reflection curves after annealing are different because of the larger interfacial width for the PS(D) / P(EMA$_{1-x}$-co-MMA$_x$) bilayer as shown in the refractive index profile in Figure 6. Another significant change of the reflection curve before and after annealing of the PS(D) / P(EMA$_{1-x}$-co-MMA$_x$) bilayer is the slight shift of the position of the total reflection angle. This effect is evident in Figure 6, from the decrease of the scattering length density ~(1-n) of the PS(D) film after annealing due to partial mixing of the two polymers. We assume that this composition, far away from the interface, corresponds to the binodal composition. Thus one calculates on the basis of the refractive index profile the binodal composition as $\phi_{B1} = 0.06 \pm 0.01$ (initial pure PS(D) layer) with respect to the P(EMA$_{1-x}$-co-MMA$_x$) volume fraction.

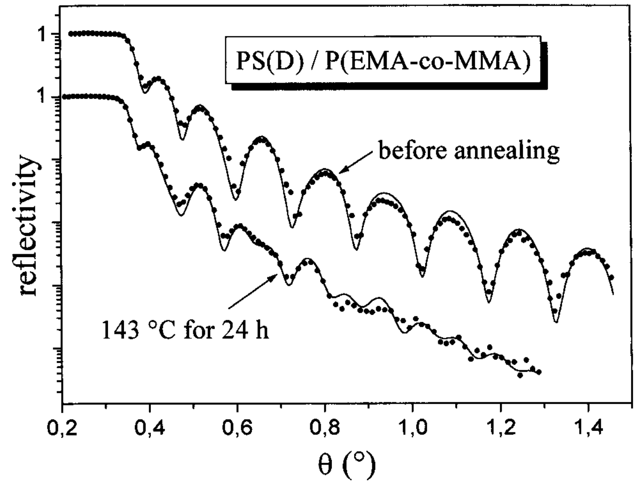

Fig. 5: Neutron reflectivity data (●) and fits (solid curves) before and after annealing of the PS(D) / P(EMA$_{1-x}$-co-MMA$_x$) bilayer sample. For better clearness, the upper curves are shifted vertical by a factor 10 on the logarithmic reflectivity scale.

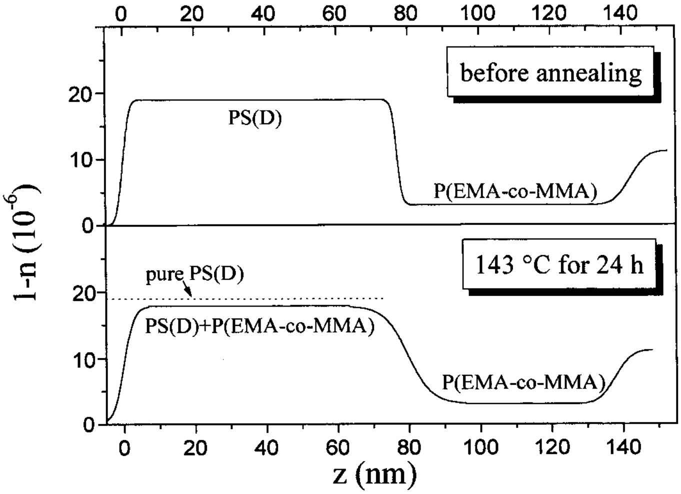

Fig. 6: Neutron refractive index profile (1-n) of the PS(D) / P(EMA$_{1-x}$-co-MMA$_x$) bilayer before and after annealing. Shown curves correspond to best fits of calculated reflection curves shown in Fig. 5.

The results are summarized in table 2 obtained by analyzing the reflectivity curves.

bilayer	a_{I0} (nm)	a_{Ie} (nm)	a_I (nm)	ϕ_{B1}	ϕ_{B2}
PS(D)/ P(EMA$_{1-x}$-co-MMA$_x$)	2.8 ± 0.4	13.2 ± 0.8	12.9 ± 0.8	0.06±0.01	>0.99
PMMA(D)/P(EMA$_{1-x}$-co-MMA$_x$)	2.4 ± 0.4	6.7 ± 0.4	6.3 ± 0.4	<0.01	>0.99

Table 2. Results of the neutron reflectometry studies on the polymer bilayers. ϕ_{B1} *is the binodal volume fraction in the initial pure PS(D) or PMMA(D) layer with respect to P(EMA*$_{1-x}$*-co-MMA*$_x$*) content after annealing.* ϕ_{B2} *is thus given by the P(EMA*$_{1-x}$*-co-MMA*$_x$*) content in the initial pure P(EMA*$_{1-x}$*-co-MMA*$_x$*) layer after annealing.*

A mean segment length of 0.73 nm which was determined for PS(D) / PMMA blends[7)] is used here for calculating χ on the basis of Eqs. (3) and (9) from the a_I values given in table 2. One obtains for PS(D) / P(EMA$_{1-x}$-co-MMA$_x$) blends an interaction parameter of $\chi = 0.0055 \pm 0.0003$ and for PMMA(D) / P(EMA$_{1-x}$-co-MMA$_x$) $\chi = 0.0140 \pm 0.0015$.

These χ values yield calculated binodal compositions which are in excellent accordance with the experimental values given in Table 2. This consistency is a very important point because capillary wave contributions to the interface widths are neglected here.

With values of the interaction parameters for PEMA/PS and PEMA/PMMA and PS/PMMA blends [9)] one can plot a similar scheme as introduced by Figure 2 in the theoretical section of this article.

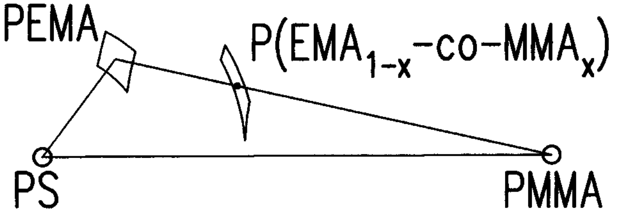

Fig. 7: Graphical representation for the interaction parameters. Distances between the polymers mirror the square root of corresponding interaction parameter. The dot in the area of P(EMA$_{1-x}$*-co-MMA*$_x$*) corresponds to the calculated position of this copolymer for a composition* $x = 0.28$.

The basis of the plot (Figure 7) is given by PS and PMMA plotted at the distance of $\sqrt{\chi}_{\mathrm{PS/PMMA}}$. The position of PEMA is defined by the distance to PS and PMMA given by $\sqrt{\chi}_{\mathrm{PEMA/PS}}$ and $\sqrt{\chi}_{\mathrm{PEMA/PMMA}}$, respectively. Geometrically, the position of PEMA is given by the intersection of two circles (centres at PS and PMMA, respectively). Additionally we insert the investigated P(EMA$_{1-x}$-co-MMA$_x$) in the same way. Due to experimental errors the intersection points degenerate to intersection areas. The position of P(EMA$_{1-x}$-co-MMA$_x$), with x = 0.28, is in excellent accordance with theory, because, the distance from PEMA to P(EMA$_{1-x}$-co-MMA$_x$) is 28% of the distance between PEMA and PMMA within experimental error. Thus Figure 7 demonstrates graphically the consistence of mean - field interaction parameters for several polymer blends utilising a novel scheme. It should be noted that the used accurate value for $\chi_{\mathrm{PEMA/PMMA}}$ was originally determined be analysing the structure of a thin film of P(EMA-block-MMA(D)) diblock copolymer by NR[19,20)] which demonstrates for this case that the interaction parameter for block copolymers and respective homopolymers seems to be the same.

The consistence of results in this work, as discussed above also justify several assumptions we have made: Effects on the interfacial width due to capillary waves [11)] are neglected here or partially included in the so called initial roughness a_{I0}. Nevertheless, several papers[7-9,11)] which utilize the same procedure as described here, demonstrate that χ parameters determined from the interfacial width values, are in excellent agreement with results obtained by other techniques. Additionally, the studies presented in this work and other published recently[7-9,11)] make no difference between hydrogenated and deuterated polymers. Bates and Wignall [21)] investigated the effect of deuteration of one component on χ in a polymer blend by SANS. However, for incompatible blends as discussed here this effect is negligible[11)]. Effects due to different microstructures of the investigated polymers are also neglected.

Finally, this article also demonstrates how the recent introduced novel scheme can be used to represent experimental results in the field of (co)polymer miscibility in a simple graphical way and enables a better understanding.

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