Investigation of the Interdiffusion between Poly(methyl methacrylate) Films by Marker Movement

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Received October 15, 1992

The interdiffusion of polymers has been investigated by various techniques, in particular also with respect to the question of fast- versus slow-mode diffusion theory (for a review see, e.g., refs 1 and 2). Those investigations were, however, mostly limited to polystyrene, poly(dimethylsiloxane), polyethylene, and more recently poly(ethylene oxide) melts, while diffusion coefficients of other polymeric materials are hardly known. In the present study we determine diffusion coefficients of poly(methyl methacrylate) (PMMA) of different molecular weights utilizing the marker technique in connection with X-ray reflectometry.[3] It allows the determination of very low diffusion coefficients in the range 10^{-14}–10^{-17} cm^2 s^{-1}, which in the present study are small due to the proximity of the glass transition temperature and due to the high molecular weights. Other techniques for the measurement of diffusion coefficients like forward recoil spectroscopy or nuclear reaction analysis are difficult to employ since PMMA is a very radiation-sensitive material. The knowledge of the diffusion coefficient of PMMA is of particular interest since PMMA is a widespread commercial material and is used as a component in various blends.

First data of diffusion coefficients of PMMA were obtained from crack healing experiments by Jud et al.[4] They used a commercial material with a large molecular weight distribution and an unknown tacticity. The interpretation of crack healing experiments with respect to interdiffusion coefficients is still not completely resolved since surface effects and segmental movement may influence mechanical data at those initial stages of interdiffusion.[5] In the marker experiments the movement of gold markers at the interface between two PMMA films of different molecular weight is used to determine the interdiffusion coefficient of the fast-moving component.[6] The position of the gold markers during interdiffusion can be followed with very good accuracy by X-ray reflectometry.[3] Using combinations of various low and high molecular weight PMMA films, one can thus determine the molecular weight dependence of the tracer diffusion coefficient of PMMA.

Experimental Section

Samples. PMMA materials are prepared by anionic polymerization and are obtained from PSS, Mainz, FRG. Samples are characterized with respect to molecular weight, glass transition temperature, temperature stability, and tacticity by gel permeation chromatography (GPC), differential scanning calorimetric (DSC), thermogravimetric analysis (TGA), and nuclear magnetic resonance (NMR). Glass transition temperatures are taken as an average from heating and cooling runs at 10 K/min. Data are summarized in Table I.

Film Preparation. Thin films of PMMA are prepared by spin coating of a toluene solution at a concentration of approximately 30 g/L on float glass (70 × 25 mm^2) to produce films of about 100-nm thickness. The surface roughness of the films is typically less than 2 nm as determined from X-ray reflectometry experiments. Subsequently, gold is evaporated onto the film (equivalent to a 2-nm homogeneous gold film on a quartz microbalance already covered with gold) which results in the formation of small particles of gold on the surface. During annealing under vacuum for 3 h at 120 °C the size of the gold particles increases to typically 4 nm as examined by electron microscopy and X-ray reflectometry.

A second film from another glass plate is floated off onto a clean water surface and transferred onto the annealed film. These double-layer films with gold in the middle are dried at 50 °C for several hours under vacuum to remove residual water and air between the two layers. Finally, a second gold layer is deposited on top of the outer PMMA film as described previously. A schematic of the sample geometry is shown in the inset of Figure 1.

Seven different samples always having the same polymer in the top layer (M_w = 980 000) but smaller molecular weight polymers in the bottom layers have been prepared and examined by X-ray reflectometry.

X-ray Measurements. X-ray reflectometry experiments are performed on a rotating-anode reflectivity setup at Mainz[7] at a wavelength of $\lambda = 0.154$ nm. Data are fitted with a simple model of homogeneous PMMA layers and error-function type interfaces. Also, for the description of the two gold layers, error functions are used as described previously.[3] The magnitude of the wave vector k is given by $k = 2\pi/\lambda \sin\theta$, where θ is the angle of incidence.

Annealing Procedure. Sample annealing is performed under vacuum conditions at different temperatures. Temperatures are measured by a thermocouple directly mounted on the sample surface. For the interdiffusion experiments of PMMA films an annealing temperature of 145 ± 1 °C is selected. X-ray experiments are performed after quenching the samples to room temperature.

Results and Discussion

The characteristic change of X-ray reflectivity curves during PMMA diffusion at different annealing times is shown in Figure 1. The periodicity of Kiessig interference fringes is mostly sensitive on the distance between the two gold layers since gold has a much larger electron density than PMMA. While it has been checked by transmission electron microscopy that during the preparation procedure small gold particles of a mean diameter of 4 nm are formed, we observe in X-ray reflectometry a "homogeneous" gold film of reduced density since the technique averages laterally over several micrometers (depending on the incident angle) and cannot resolve the individual gold particles. The resolution in the direction perpendicular to the surface is, however, much better, and the mean scattering density profile as well as the net movement of the gold layers can be resolved with a resolution much better than 1 nm. Here, sample preparation causes restrictions since, for instance, the surface roughness of films is also within this range. The thickness of the gold layer, on the other hand, stays approximately constant within the time scale of the annealing experiments.

Reflectivity data are interpreted in terms of a simple layer model indicated in the inset of Figure 1. Model fits give a reasonable description of the periodicity of reflectivity curves. We did not attempt to also model the gold layers in detail, which would improve the quality of the fits considerably.[3] From the distance between gold layers the gold marker movement of the buried gold particles is deduced which is plotted in Figure 2 for samples of different molecular weights. After the first annealing we

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0024-9297/93/2226-2134$04.00/0

Table I
Characteristic Data of PMMA Materials Used in This Work and Results of Interdiffusion Experiments between Films of Different Molecular Weights of PMMA at T = 145 °C[a]

	GPC		TGA	DSC	NMR			
PMMA no.	M_w	M_w/M_n	T_{dec} (°C)	T_g (°C)	iso/syndio (%)	τ_R (s)	τ_d (s)	D^* (10^{-16} cm² s⁻¹)
1	12 900	1.04	280	113.6	5/56			>300
2	23 800	1.07		113.5		0.72	6.38	73.2
3	37 000	1.04		114.8	4/40	4.84	67.2	10.8
4	85 500	1.05	280	116.4	5/38	22.2	711	2.36
5	194 000	1.03		116.3	6/37	238	17300	0.22
6	491 000	1.06		118.1	5/45	>500	>90000	<0.1
7	980 000	1.07	240	116.9	4/41			

[a] Rouse time, τ_R, and disengagement time, τ_d, are explained in the text.

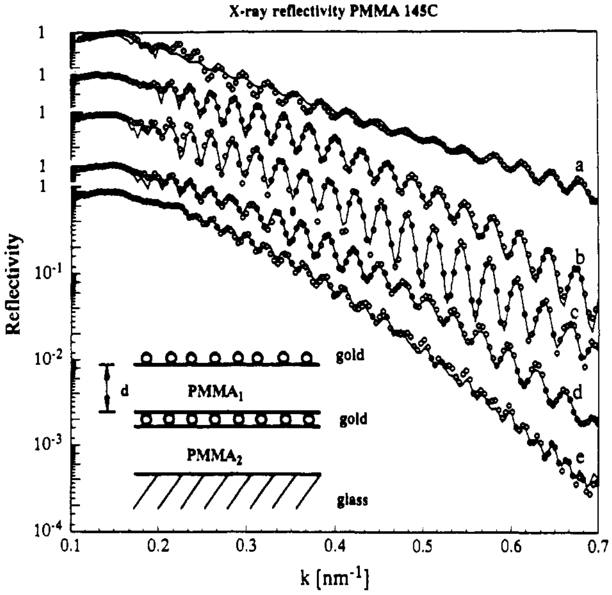

Figure 1. Comparison of measured reflectivity curves (○) of a PMMA sample (37K vs 980K) with model fits (—) at different annealing times: (a) t = 0 min, (b) t = 7 min, (c) t = 16 min, (d) t = 36 min, (e) t = 1600 min. A schematic drawing of the layer samples used in the experiments is shown in the inset.

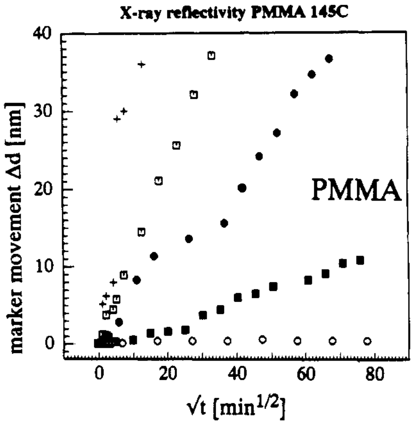

Figure 2. Displacement Δd of the gold markers (or thickness variation of the upper PMMA film) versus square root of time of five samples: (+) M_w = 23 800, (□) M_w = 37 000, (●) M_w = 85 500, (■) M_w = 194 000, (○) M_w = 980 000. The molecular weight of the upper film is always 980K, while the molecular weights of the lower films have been changed to the values indicated.

observe film thickness relaxations and a movement of gold particles over a distance corresponding to their radius into the films. Those initial stages of annealing have been omitted. As a check also the combination 980K vs 980K PMMA is shown were one does not expect a net mass flow across the interface due to the identical mobility of chains on both sides.

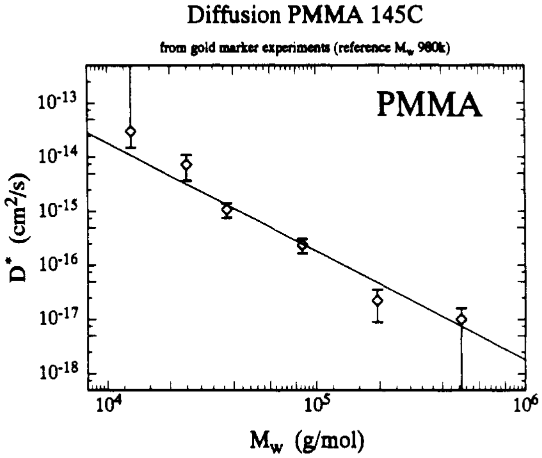

Figure 3. Measured tracer diffusion coefficients (D^*) of PMMA plotted against PMMA molecular weight at T = 145 °C. A theoretical curve with a slope of α = 2 is also indicated by the solid line.

Following a treatment within the fast-mode diffusion theory[6] and reptation arguments,[8] one would expect for PMMA films with largely different molecular weights and for times larger than the disengagement time, τ_d, of the faster component a net mass flow across the interface which directly yields the tracer diffusion coefficient of the fast-moving component. This mass flow is monitored by the movement of gold particles situated at the interface, Δd, while the gold particles at the surface do not move into the sample. The slope in Figure 2 is thus directly related to the square root of the tracer diffusion coefficient, D^*, of the fast-moving component:

$$\Delta d = C(D^*t)^{1/2}$$

C is a constant which depends on the ratio of the molecular weights of the components.[6] For the investigated samples it ranges from 0.28 to 0.48 for the high and low molecular weight materials, respectively.

Tracer diffusion coefficients of PMMA of different molecular weight at 145 °C measured against PMMA of 980K molecular weight are shown in Figure 3 and can be fitted well with a power law $D^* = kM_w^{-\alpha}$, $k = 1.8 \times 10^{-6}$ cm² s⁻¹ g⁻¹ mol, and α = 2.0 (±0.2) also plotted as a solid line in Figure 3. Values are given in Table I where also Rouse time, τ_R, and disengagement time of the fast-component, τ_d, have been estimated on the basis of measured diffusion coefficients. Since the errors in the values of samples 1 and 6 are large, D^* given can essentially be taken as lower and upper limits for the diffusion coefficients. It should also be kept in mind that tracer diffusion coefficients may strongly depend on the matrix molecular weight.[1,2,9] The entanglement molecular weight of PMMA ($M_c \approx 30\,000$) is, however, much smaller than the reference molecular weight (980 000) in the present study, and one can assume that constraint-release contributions are negligible. Thus tube renewal should not occur, and one may expect reptation behavior, which is consistent with our experiments. With PMMA, the diffusion coefficients may in addition also depend on tacticity and water context (plasticizer), which has been noted earlier.[4]

For a comparison with other experiments one has to be careful comparing diffusion coefficients at a given temperature since glass transition temperatures of different samples may be quite different. Thus diffusion coefficients reported by Jud et al.[4] are larger which one may attribute to the lower glass transition temperature (101 °C) of their samples. This is also true for the diffusion coefficient of deuterated PMMA (H_{w} = 146 000) in prononated PMMA (88 000) recently reported by Van Alsten and Lustig[10] where a glass transition temperature of 106 °C is quoted. Reducing those data to a constant distance from T_{g} on the basis of activation energies also reported by those authors yields diffusivities which are in reasonable agreement with Figure 3. Further work is in progress to also measure activation energies and matrix effects for PMMA diffusion.

Acknowledgment. We acknowledge the stimulating discussions with Prof. H. H. Kausch and Prof. E. W. Fischer as well as the help of Dr. G. Lieser during the electron microscopy investigations and of B. Schramm during the film preparations. This work was partially supported by BMFT.

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