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Spin coating as a method for polymer molecular weight determination

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Summary

The spin coating process was investigated using solutions of polystyrene dissolved in toluene. The residual film thickness depends not only on the spinning velocity and concentration, but also on molecular weight. Specific scaling exponents were determined. The molecular weight dependence was investigated in detail to reveal the type of molecular weight average. This enables a fast determination of the molecular weight by use of spin coating. The use of model molecular weight distributions yields a relation to number M_n and weight M_w average molecular weight.

Introduction

Spin coating has been accepted as the best coating method for obtaining films over a wide range of thicknesses (1), typically 30 to 2000 nm. It is accomplished by covering the substrate with a polymer solution and rotating it at a constant spinning velocity until the solvent has evaporated. In particular spin coated films are uniform in thickness and smooth over large areas (1, 2, 3). The spin coating process is thus extensively used in microelectronics for coating planar surfaces. In polymer research it is used for preparing single films which are subsequently floated onto each other (3). Such double layers are excellent model systems investigating polymer/polymer interfaces (3, 4, 5). Knowledge of the parameters for affecting the film thickness are of crucial importance for controlling film preparation. The only known studies of the influence of molecular weight on film thickness are the qualitative results of Weill et al. (1, 6). Weill et al. investigated solutions of polymethylmethacrylate (PMMA) dissolved in trichlorethylene where two PMMA samples with different molecular weight distributions were used. As it will be shown in this article for solutions of polystyrene (PS) dissolved in toluene the entire range of the appropriated molecular weight distribution has to be considered. Finally the results given in this article allow a rapid determination of molecular weight for PS by the use of spin coating via a thickness measurement of the residual film.

Experimental

For this investigation, several samples of PS (see table 1) were employed in order to obtain the dependence of the residual film thickness as a function of spinning velocity, concentration and molecular weight.. The PS samples were synthesised at the Max - Planck - Institut for polymer research.

sample	1	2	3	4	5	6	7	8
M_w (kg/mol)	60	106	253	440	712	111	719	271
M_w/M_n	1.07	1.04	1.04	1.04	1.04	1.06	1.11	2.83
polymerisation	anionic							rad.

Table 1: Molecular characteristics of the used PS samples.

The molecular weight distributions were determined with gel permeation chromatography (7). The PS samples were dissolved in toluene and stirred for at least one hour. Subsequently the solutions were put on float glass substrates 2.5 x 2.5 cm^2 (see figure 1) which were then rotated for 30 seconds at a constant spinning velocity until the solvent evaporated. Additional experiments demonstrated that the residual film thicknesses were not affected by a specific amount of solution deposited onto the glass substrate. However, for the experiments presented here, the diameter of the solution spot was not less than 1 cm. Thickness variations of the residual film were observed only in the vicinity of the edges. The homogenous central region of approximately 1.5 x 1.5 cm^2 showed no systematic variations of the film thickness. Measurements at different places in the central region yield a mean value and a typical error of 3 nm for the film thickness. Neutron and X-ray reflection experiments have also demonstrated that spin coated films are homogenous over large areas (3).

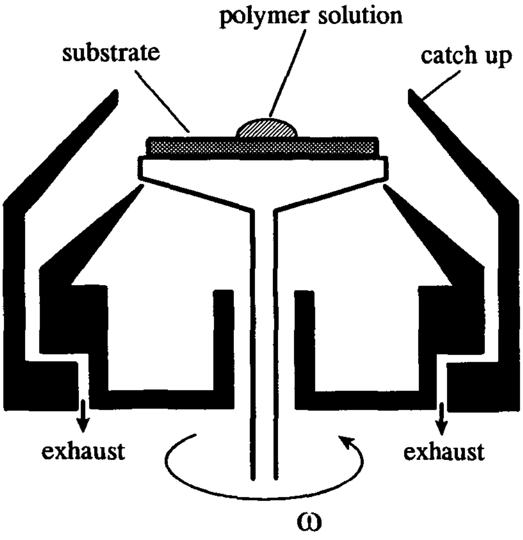

Fig. 1: Schematic diagram of a typical spin coating system.

The significant parameters affecting for the residual film thickness are the concentration of the solution, the spinning velocity (8) and the molecular weight as discussed in this article. Film thicknesses were determined by analysing the profile of a groove in the films with a commercial α - stepper (α - step 200, Tencor Instruments) utilizing a probing needle which was pressed against the sample with a force of 3x10^{-5} N.

Results and Discussion

Dependence of the film thickness on the spinning velocity

Sample 3 was used to prepare a solution with a concentration of 20 g/l. Several spinning velocities ω were programmed into the spin coater. Results are shown in figure 2.

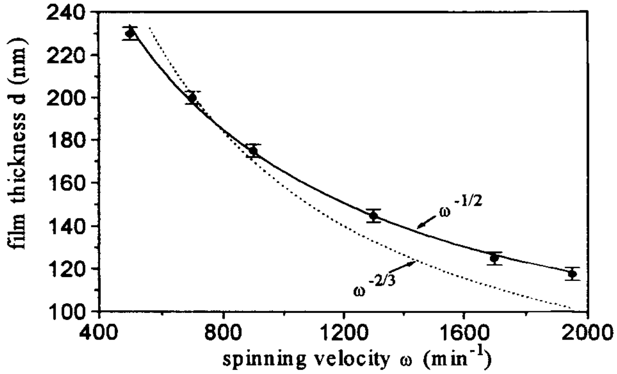

Fig. 2: Thicknesses of spin coated films as a function of spinning velocity utilising sample 3 dissolved in toluene with a concentration of 20 g/l. Fitting curves represent different scaling exponents for the spinning velocity dependence as predicted by theory. Details are provided in the text.

Initial theoretical approaches (9) predicted a relation (equation 1) connecting film thickness d with spinning velocity ω, viscosity η and solvent evaporation rate E:

$$d \sim \eta^{1/3} \omega^{-2/3} E^{1/3} \qquad (1)$$

Fitting the experimental values shown in figure 2 to the dependence on spinning velocity in equation 1 yields significant deviations. The reason for these deviations is an additional dependence of the evaporation rate E on the spinning velocity calculated by Bornside et al. (10):

$$E \sim \omega^{1/2} \qquad (2)$$

Combining equation (1) with (2) yields:

$$d \sim \omega^{-1/2} \qquad (3)$$

Utilising equation (3) one obtains:

$$d = 118.0nm \left(\frac{1950 \,\mathrm{min}^{-1}}{\omega} \right)^{1/2} \qquad (4)$$

The scaling behaviour in equation (3) was also found by other experimental groups (1, 6, 8, 11) utilising different polymers and solvents, and seems to represent a general relation for spin coated films.

Dependence of the film thickness on the concentration of the solution and the molecular weight of the polymer

To investigate the influence of solution concentration on film thickness, several solutions with different concentrations were prepared utilising PS samples 2 and 5. Films were spin coated at a spinning velocity of $\omega = 1950\ \mathrm{min}^{-1}$. Results of the thickness determinations are shown in figure 3.

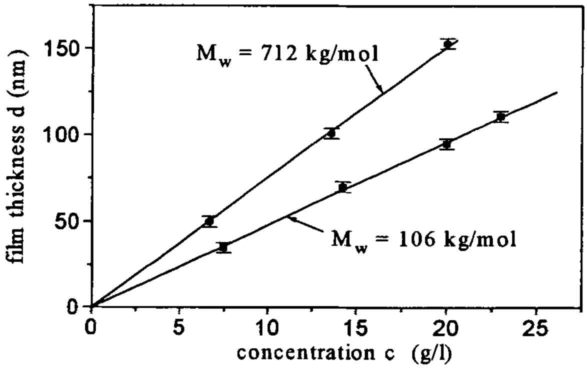

Fig. 3: Film thickness as a function of concentration for sample 2 and 5 prepared at a spinning velocity of $\omega = 1950\ min^{-1}$. The solid lines represent fit curves to a proportional relation of film thickness and concentration c.

The fits to a proportional relation of film thickness and concentration (figure 3) yield

$$d = 96.2nm\left(\frac{c}{20g/l}\right) \tag{5}$$

$$d = 151.4nm\left(\frac{c}{20g/l}\right) \tag{6}$$

for M_w = 106 kg/mol and M_w = 712 kg/mol respectively. Assuming that film thickness scales with molecular weight

$$d \sim M_w^{\nu} \tag{7}$$

and one obtains from equation 5 and 6 an exponent of $\nu = 1/4$. Using samples 1 to 5 the scaling of film thickness with molecular weight can be verified in addition to equation 5 and 6 (see figure 4). Combining these results yields the following relation for polystyrene dissolved in toluene:

$$d = 93.5nm\left(\frac{1950\mathrm{min}^{-1}}{\omega}\right)\left(\frac{c}{20gl^{-1}}\right)\left(\frac{M_W}{100kgmol^{-1}}\right)^{\frac{1}{4}} \tag{8}$$

A limitation of equation 8 appears for concentrations higher than approximately 25 g/l when the molecular weight of the polymer is greater than approximately 10^3 kg/mol (12). Additionally, a lower limit arises for small concentrations when the expected film thickness is comparable to the radius of gyration.

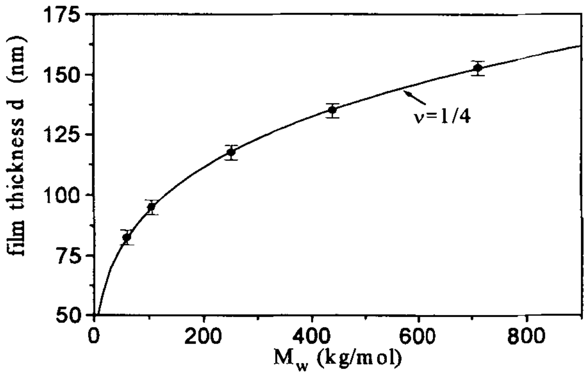

Fig. 4: Scaling of film thickness with molecular weight utilising solutions of samples 1 to 5 dissolved in toluene with concentrations of 20 g/l. Spin coated films were prepared at a spinning velocity of $\omega = 1950$ min^{-1}. The solid line represents a fit to equation 7.

Keeping in mind that different molecular weight averages exist the assumption in equation 6 and 7 that film thickness scales with the weight - average molecular weight M_w was an arbitrary choice. However the utilised anionic synthesised polymer samples were nearly monodisperse and the differences for the various types of molecular weight averages are negligible. In order to obtain the type of molecular weight average bidisperse polymer samples were prepared by blending samples 6 and 7 with various compositions. Table 4 shows the amounts m_6 and m_7 used of sample 6 and 7, respectively. The total mass of polymer m is given as the sum of m_6 and m_7. To dissolve the bidisperse blends 3 ml toluene were used.

m_6 (mg)	m_7 (mg)	c (g/l)	n	d (nm)	M_{sp} (kg/mol)
1.8	48.4	16.73	0.806	127 ± 3	660 ± 62
2.7	47.5	16.80	0.732	127 ± 3	649 ± 61
4.5	44.7	16.40	0.605	120 ± 3	570 ± 57
6.5	43.3	16.60	0.507	120 ± 3	543 ± 54
8.4	41.5	16.63	0.433	115 ± 3	455 ± 47
10.0	39.3	16.43	0.378	117 ± 3	511 ± 52
11.7	37.5	16.40	0.331	111 ± 3	417 ± 45
14.7	34.8	16.50	0.268	110 ± 3	393 ± 43
20.0	29.6	16.53	0.186	105 ± 3	324 ± 37
25.0	24.8	16.60	0.133	100 ± 3	262 ± 31
30.0	20.8	16.93	0.097	101 ± 3	252 ± 30
35.5	14.5	16.67	0.059	90 ± 3	169 ± 23
39.7	10.0	16.57	0.037	83 ± 3	125 ± 18
45.0	4.7	16.57	0.016	80 ± 3	108 ± 16

Table 2: Compositions and results for bidisperse samples utilising blends of sample 6 and 7. Films were prepared at a spinning velocity of 1900 min^{-1}.

The composition n is the relative number of chains corresponding to the longer chains:

$$n = \frac{\dfrac{m_7}{719 kg/mol}}{\dfrac{m_6}{111 kg/mol} + \dfrac{m_7}{719 kg/mol}} \tag{9}$$

Films were spin coated at a spinning velocity of $\omega = 1900$ min^{-1}. Utilising equation 7 yield the molecular weight M_{sp} as a function of composition n (see figure 5) where M_{sp} represents the type of molecular weight which is accessible by spin coating.

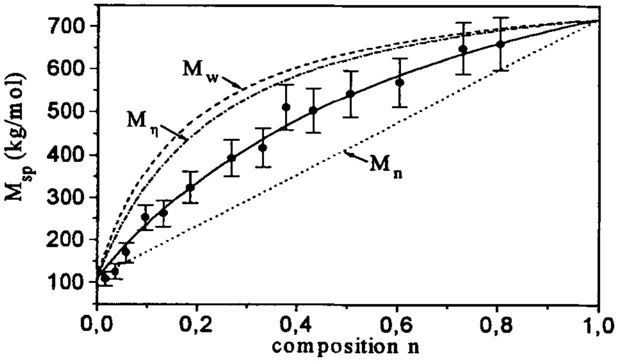

Fig. 5: Molecular weight M_{sp} of bidisperse samples obtained by spin coating as a function of composition n. Several molecular weight averages are shown as explained in the text. The solid line represents the best fit to the data utilising equation 10.

Utilising the definition of equation 9 for a bidisperse polymer blend the molecular weight averages are given by

$$M_\beta = \frac{(1-n)111^{\beta+1} + n719^{\beta+1}}{(1-n)111^{\beta} + n719^{\beta}} kg/mol \tag{10}$$

where $\beta = 0, 1$ represent the number - average molecular weight, M_n, and weight - average molecular weight, M_w, respectively. Further moments of the molecular weight can be defined. For instance, the z - average molecular weight is represented by $\beta = 2$ in equation 10. In the range between M_n and M_w the viscosity average molecular weight, M_η occurs:

$$M_\eta = \left(\frac{(1-n)111^{a+1} + n719^{a+1}}{(1-n)111 + n719} \right)^{1/a} kg/mol \tag{11}$$

The parameter a in equation 11 depends on the polymer and solvent used. For PS dissolved in toluene one finds a literature value for a of 0.73 (13). However, the viscosity average molecular weight does not describe the data obtained from spin coating experiments (see figure 5). Neither do the number - average molecular weight or the weight - average molecular weight. Utilising equation 10 and fitting the parameter β one obtains $\beta = 0.5$ as the best fit to the data shown in figure 5. For this exponent, the enhanced form of equation 10 for general molecular weight distributions is given by

$$M_{sp} = \frac{\int_0^\infty M^{1.5} N(M) dM}{\int_0^\infty M^{0.5} N(M) dM} \tag{12}$$

to calculate the molecular weight obtainable by spin coating. The function N(M) in equation 12 gives the number of chains with a molecular weight M. Simple model functions for N(M) give relations connecting M_{sp} to M_n and M_w. The following function

$$N(M) = M^r e^{-bM} \tag{13}$$

yields $$M_{sp} = \frac{M_n + M_w}{2} \tag{14}$$

for r ≥ 0. In particular the value r = 0 represents the Shultz - Flory distribution for the molecular weight. Considering a stretched exponential distribution

$$N(M) = e^{-bM^\delta} \tag{15}$$

the molecular weight averages are given by

$$M_n = \frac{\Gamma(2/\delta)}{\Gamma(1/\delta)} \frac{1}{b^{1/\delta}}, \quad M_w = \frac{\Gamma(3/\delta)}{\Gamma(2/\delta)} \frac{1}{b^{1/\delta}} \text{ and } M_{sp} = \frac{\Gamma(2.5/\delta)}{\Gamma(1.5/\delta)} \frac{1}{b^{1/\delta}} \tag{16}$$

where Γ(x) is the Gamma function. Comparing the mean value of M_n and M_w with M_{sp} for several δ values one finds that equation 14 is a good approximation. The deviations are typically less than 5 %. It should be noted that the equations 16 yield

$$\frac{M_n + M_w}{2} < M_{sp} \text{ for } \frac{M_w}{M_n} < 2 \quad \text{and} \quad \frac{M_n + M_w}{2} > M_{sp} \text{ for } \frac{M_w}{M_n} > 2.$$

To demonstrate the validity of equation 12 sample 8, which has a broad molecular weight distribution (shown in figure 6) with M_n = 96 kg/mol and M_w = 271 kg/mol was investigated.

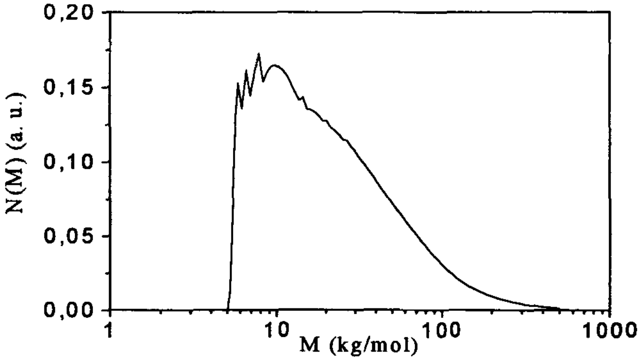

Fig. 6: Molecular weight distribution of sample 8.

Films were spin coated using a solution of sample 8 dissolved in toluene with a concentration of 16.17 g/l. Two different spinning velocities were used. The residual film thicknesses enable the experimental determination of the molecular weight utilising equation 8. Results are given in table 3.

ω (min^{-1})	d (nm)	M_{sp} (kg/mol) experimental	M_{sp} (kg/mol) calculated	$\frac{M_n + M_w}{2}$ (kg/mol)
800	135 ± 3	171 ± 15	167	183
1900	88 ± 3	174 ± 24	167	183

Table 3: Results of spin coating experiments utilising sample 8.

Table 3 also shows M_{sp} calculated utilising equation 12 and the molecular weight distribution N(M) from figure 6. The nice accordance demonstrates the possibility of a fast determination of molecular weight by using spin coating. However, these investigations concerning the molecular weight are restricted to PS dissolved in toluene. A comprehensive theoretical understanding of the molecular weight dependence is still missing. The semi - empirical equation 1 gives rise to the molecular weight dependence via the viscosity. Further studies are necessary to enhance the understanding of the spin coating process. In particular connections to the Mark - Houwink - Staudinger - equation should also be investigated (12).

Acknowledgement

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