Macromolecules

Volume 37, Number 24 November 30, 2004

Communications to the Editor

Glass Transition Temperature in Thin Polymer Films Determined by Thermal Discharge in X-ray Photoelectron Spectroscopy

Jörn Erichsen, Kai Dolgner,
Vladimir Zaporojtchenko, and Franz Faupel*

Lehrstuhl für Materialverbunde, Technische Fakultät,
Kiel University, Kaiserstr. 2, 24143 Kiel, Germany

Received January 18, 2004
Revised Manuscript Received August 19, 2004

Introduction. Recently, there is much interest in the dynamics in thin polymer films.[1] Keddie et al.[2] first observed a depression of the glass transition temperature T_g in thin supported polystyrene films according to the empirical relationship

$$T_g = T_g^{\infty} - \left(\frac{a}{h}\right)^{\delta} \qquad (1)$$

where h is the film thickness and a and δ are parameters. During the past years several methods have been applied to measure T_g in thin films.[1] Most of them are based on a thermal expansion measurement. Unfortunately, the extent of the T_g depression is still discussed very controversially. Diffusion studies[3] and recent differential thermal calorimetry (DSC) measurements even suggest a lack of any T_g depression.[4,5] Recently,[6,7] we reported an application of X-ray photoelectron spectroscopy to determine T_g at the polymer surface, which is based on the embedding of Au nanoclusters in polymer.

Here we report a new approach to determine T_g in thin films. Our method takes advantage of the positive charging of polymeric films induced by the photoelectron emission. The charging is reflected in a line shift in the XPS spectra.[8] The glass transition is monitored via the concomitant discharge of the polymer film due to the disorientation of the dipoles by the motion of main chain segments and also partly due to the self-motion of space charges. The latter is accompanied by recombination with thermally generated carriers at high temperatures and leads to change in the electrical conductivity. These discharge phenomena are well-known from thermally stimulated discharge (TSD) measurements on bulk polymers, where a clear correlation with T_g has been observed.[9] The present method measures T_g in the bulk of thin films and is hence complementary to our other method, which is based on the embedding of nanoclusters and measures T_g at the surface.[6,7] Our results show a decrease in the glass transition temperature with decreasing film thickness in almost quantitative agreement with the Keddie−Jones−Cory equation.

Experimental Section. The experiments where carried out using monodisperse polystyrenes (PS) samples with molecular weights of M_w 3.7 kg/mol and 1000 kg/mol (M_w/M_n < 1.06, Aldrich Inc.). These polystyrenes are terminated with *sec*-butyl groups. Polystyrene films were prepared by solving the polymer powder in toluene and spin-coating the solution onto polished silicon wafers with their native oxide layer. The thickness of the films was measured with a profilometer (Stylus DEKTAK 8000, Veeco Ins. Inc.). For XPS investigations small samples of about 1 cm^2 were broken from a polymer-coated Si wafer. These samples were bonded onto stainless steel sample holders with a graphite glue to increase the thermal contact. To be sure that all solvent and water were evaporated and the polymer films were in a well-defined relaxed state, all samples were annealed in the UHV system at a temperature $T = T_g(\text{bulk}) + 30$ K for at least 3 h and then cooled to room temperature with a constant cooling rate of 1 K/min prior to XPS measurement. To monitor the temperature during the experiment, K-type thermocouples were mounted directly on the sample holder's surface close to the sample. Prior to the measurements the surface temperature was determined with another thermocouple directly mounted on the surface of a typical sample. For a heating rate of 1 K/min it was observed that the temperature difference between the

---

* Corresponding author. E-mail: ff@tf.uni-kiel.de.

10.1021/ma049870h CCC: $27.50

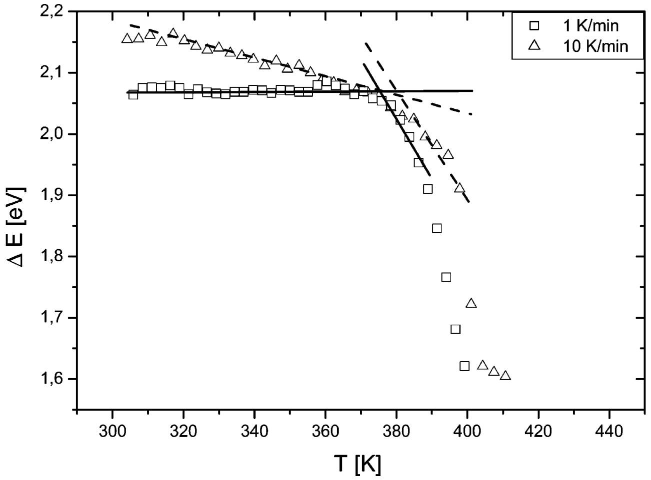

Figure 1. Shift of the binding energy E_B as a function of temperature during heating at a constant rates of 1 and 10 K/min, respectively, for PS film of $M_w = 1000$ kg/mol. The film is 300 nm thick and hence shows bulklike behavior. Discharging is reflected in a decrease of E_B. The discharge temperature T_d was determined as the temperature of the intersection point between two linear fits as indicated.

polymer surface and the thermocouples on the sample holder is always less than 1.5 K. This information was used for calibration of the thermocouple used for the experiments.

XPS measurements were carried out under normal electron emission. The system is equipped with a double anode (VG Microtech XR3E2) and a hemispherical analysator (VSW Instruments EA 125). The experiments were performed with the Al anode at a typical power of 270 W (15 kV, 18 mA). The spectra were taken with the program SPECTRA. Spectra of the C 1s line with a pass energy of 100 and 20 eV were measured during each series. After a Shirley background correction peaks were fitted. This was performed with the VAMAS data file format processing software CasaXPS. The bulk glass transition of the polymers was determined with DSC (Perkin-Elmer, Pyris 1) with different heating rates using the second run after cooling at 1 K/min.

Results and Discussion. For polymeric films on a conducting substrate, the sample charge is a function of X-ray power as well as of the film thickness. It takes several minutes to reach equilibrium (saturation value of the XPS peak shift). This may even be used to estimate the polymer thickness.[10] The influence of the substrate temperature on the peak shift of a typical PS film is shown in Figure 1.

The energy shift ΔE related to the C 1s binding energy of 284.9 eV without charging is plotted vs temperature. For temperatures below the bulk glass transition temperature T_g no significant change in ΔE is observed. At T_g, however, ΔE decreases strongly. A discharge temperature T_d was determined as the temperature of the intersection point between two linear fits. There is some uncertainty concerning the fitting range above T_g. This leads to an error in T_d of typically ±3−4 K.

The T_d values for monodisperse polystyrenes (PS) samples with molecular weights of M_w 3.7 and 1000 kg/mol together with T_g(bulk) from DSC measurement and T_g(surface) from our cluster embedding method[6,7] are shown in Table 1. The T_d values agree with T_g(bulk) within error margins and are above the values of T_g(surface).

Table 1. Discharge Temperatures T_d for Both Molecular Weights Obtained at a Heating Rate of 1 K/min[a]

	T_d/K	T_g(bulk)/K	T_g(surface)/K
$M_w = 3.7$ kg/mol	354 ± 4	348 ± 1	345 ± 3
$M_w = 1000$ kg/mol	377 ± 4	374 ± 1	368 ± 3
$M_w = 1000$ kg/mol with graphite	376 ± 3		

[a] For comparison the bulk and the surface glass transition temperatures are also shown. The surface of one sample was contacted with graphite. The discharge temperature of this sample is identical to the noncontacted ones. Therefore, a surface effect on T_d can be ruled out.

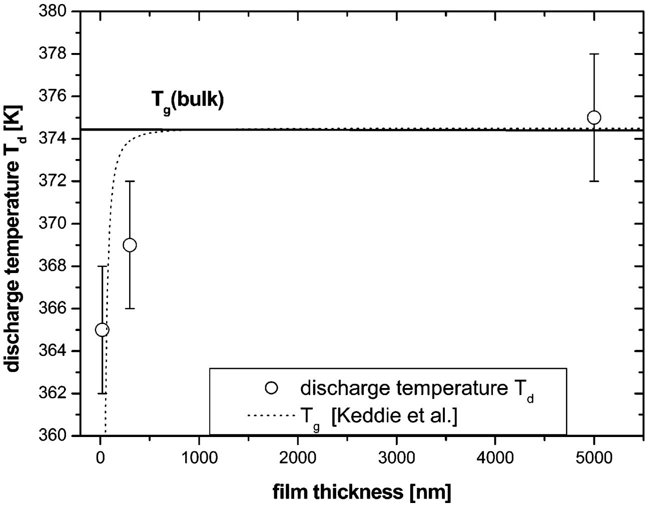

Figure 2. Thickness dependence of the discharge temperature as determined in the present paper and according to the Keddie−Jones−Cory equation. The decreases of T_d for thinner films is obvious.

To clarify whether T_d is a bulk or a surface property, we performed discharge experiments with samples, where the edges of the surface were grounded with graphite and the film was bombarded with 1 keV Ar^+ ions. No change is seen in T_d after contacting the surface with graphite. Also, the peak shift of ion etched PS surfaces shows no difference to that of the untreated one. In contrast, a significant increase of the surface T_g was observed for ion treatment by means of the embedding methods.[11] Details about this method, which detects the glass transition at the surface, can be found in refs 6 and 7. The present measurements clearly show that T_d reflects a bulk and not a surface property.

As a further test to demonstrate that our novel method detects the glass transition in the bulk of thin films, we took the well-known thickness dependence of T_g for polystyrene films described by the Keddie−Johnes−Cory[2] equation for comparison and measured T_g at three thicknesses (very small, intermediate, and bulklike). The results are shown in Figure 2 together with T_g(bulk) and the Kedie−Johnes−Cory equation. The parameters a and δ (see eq 1) were taken from Keddi et al.[2] The agreement with the empirical Keddie−Johnes−Cory equation is quite good. The small but significant depression of T_g with decreasing film thickness is well reflected in our date points.

In conclusion, using polystyrene on a silicon substrate as a model system, we introduced a novel technique to measure the glass transition in thin polymer films. The technique is based on X-ray photoelectron spectroscopy, which is a widely available method in surface and thin film science. It takes advantage of the charging of dielectric samples due to photoelectron emission. The glass transition is detected via thermal discharging. By (a) making the surface conducting, (b) cross-linking the surface by means of ion bombardment, and (c) by measuring the film thickness dependence and comparing with the prediction of Keddie−Johnes−Cory equation, we demonstrated that our technique is not sensitive to the surface glass transition but measures the glass transition in the bulk of the thin films. The technique is thus complementary to our earlier approach to measure the glass transition at the surface via embedding of gold nanoclusters. Since both techniques are based on in situ XPS measurements, it is possible to measure simultaneously, using one and the same sample, the glass transition at the surface and in the bulk. To do so, one simply has to cover half of the sample with a mask during evaporation of the gold clusters and to measure both peak shift and intensities. Thus, systematic errors (in absolute temperature, sample history, heating rate, etc.), which generally make a comparison of bulk and surface glass transition temperatures difficult, can be largely ruled out.

Acknowledgment. The authors thank Rainer Adelung for stimulation discussions concerning charge transport in dielectrics.

References and Notes

(1) Forrest, J. A. *Eur. Phys. J. E* **2002**, *8*, 261−266.
(2) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Europhys. Lett.* **1994**, *27*, 59−64.
(3) Pu, Y.; White, H.; Rafailovich, M. H.; Sokolov, J.; Patel, A.; White, C.; Wu, W.-H.; Zaitsev, V.; Schwarz, S. A. *Macromolecules* **2001**, *34*, 8518−8522.
(4) Efremov, M. Y.; Warren, J. T.; Olson, E. A.; Zhang, M.; Kwan, A. T.; Allen, L. H. *Macromolecules* **2002**, *35*, 1481−1483.
(5) Efremov, M. Y.; Olson, E. A.; Zhang, M.; Zhang, Z.; Allen, L. H. *Phys. Rev. Lett.* **2003**, *91*, 085703.
(6) Zaporojtchenko, V.; Strunskus, T.; Erichsen, J.; Faupel, F. *Macromolecules* **2001**, *34*, 1125−1127.
(7) Erichsen, J.; Schürmann, U.; Kanzow, J.; Dolgner, K.; Günther-Schade, K.; Strunskus, T.; Zaporojtchenko, V.; Faupel, F. *Macromolecules* **2004**, *37*, 1831−1838.
(8) Seah, M. P. In *Practical Surface Analysis*; Briggs, D., Seah, M. P., Eds.; Wiley Interscience: New York, 1990; pp 541−550.
(9) van Turnhout, J. In *Electrets*; Sessler, G., Ed.; Springer: Berlin, 1987.
(10) Cros, A. *J. Electron Spectrosc. Relat. Phenom.* **1992**, *59*, 1−4.
(11) Zaporojtchenko, V.; Zekonyte, J.; Erichsen, J.; Faupel, F. *NIM B* **2003**, *208*, 155−160.

MA049870H