Solvent retention in thin polymer films studied by gas chromatography

J. García-Turiel · B. Jérôme

Abstract  Thin polystyrene films were produced by spin coating from solutions in toluene. The amount of solvent retained in the films after drying for different times was measured using gas chromatography. Whereas for thicker films (thickness > 200 nm), the relative amount of solvent in the films is less than a few percent, the proportion of toluene increases significantly in thinner films. The thickness dependence of the mass of retained solvent shows that the solvent is mainly retained at the polymer–substrate interface. The solvent desorption rate exhibits no variation on the film thickness.

Keywords  Polymer films · Solvent desorption · Gas chromatography · Polystyrene

Introduction

Although most mechanical applications of polymers take advantage of their bulk properties, there are numerous technologies based on ultra thin and thin polymers. For example, they are used as resists and interlayer dielectrics in microelectronics fabrication, alignment layers in liquid crystal displays, and lubricants in magnetic information storage devices. In these applications, the polymer chain orientation and state of organization play an important role in determining the final properties of the films [1].

Thin films are usually fabricated by spin-casting. In this coating procedure, a polymer solution is first deposited on the substrate, and the substrate is then accelerated rapidly. Owing to the centrifugal force, a film of the solution is formed, and the excess is ejected off the edge of the substrate. The film continues to thin slowly until disjoining pressure effects causing the film to reach an equilibrium thickness or until it turns solid-like due to a dramatic rise in viscosity resulting from the solvent evaporation. The final thinning of the film is then due solely to solvent evaporation [2]. Most of the solvent evaporates during the last step of the spin-coating, but it is known that some solvent is still present in the films at the end of the spin-coating [1, 3, 4] and that the polymer chains are quenched in a nonequilibrated state [5–8]. Spin-coated films are therefore generally annealed above the glass transition temperature of the polymer to dry the films and let the polymer relax to equilibrium. Whereas solvent loss during this drying step (with respect to the initial solvent content) has been extensively studied [3, 4, 9–15], there is hardly any information available on the absolute amount of solvent left in the films.

There is however a number of reported results suggesting that some solvent is retained in dried films. In
absorption/desorption experiments of toluene in several methacrylate polymer films, Saby-Dubreuil et al. [16] observed that some of the absorbed toluene remains trapped in the films even after extensive drying. The presence of solvent in films has also been detected through some changes in the film properties [17, 18].

A striking result is the fact that the glass transition temperature \( T_g \) of annealed stereo-regular poly(methyl methacrylate) films strongly depends on the solvent used for spin-coating them [19]. \( T_g \) is either larger or smaller than the transition temperature in bulk, depending on the solvent used. This effect was interpreted as arising from different conformations of the polymer chains persisting even after annealing. The presence of solvent retained in the films could be another explanation. Finally, the mechanical adhesion of annealed diblock copolymer films on the supporting substrate was also observed to depend on the solvent used for spin-coating [20], suggesting again a possible presence of solvent retained after drying.

Besides the question of whether and how much solvent is retained, one should wonder where the solvent is located in the films. Some of the results mentioned above suggest that the solvent could be segregated at the polymer/substrate interface [19, 20]. Water absorbed in films of different polymers has also been shown to be located at the polymer/substrate interface [21–25]. Another relevant question is the dependence of the amount of retained solvent with the film thickness. Indeed, properties of polymer films, such as the glass transition temperature and the molecular dynamics, are known to change as the film thickness decreases below a few 100 nm [26–29].

We have therefore studied the amount of solvent retained in polystyrene (PS) films spin-coated from a solution in toluene as a function of film thickness in the range of 15–500 nm. The absolute amounts of retained solvent were investigated using gas chromatography (GC), which appears to be a very useful technique to perform residual solvent analysis, even for the minute volumes of our thin films.

In the following section, we present how we prepared the samples and measured the amount of solvent retained after drying. In “Results and discussion,” we show our results on the amount of toluene retained in PS films as a function of film thickness and drying time. We discuss the implications of these results, showing that there is a significant proportion of solvent present in ultra-thin films and that this solvent is mainly retained at the interface with the substrate. We also find that the desorption rate is independent of film thickness.

Experimental section

Sample preparation

PS films were prepared by spin-coating from solutions of PS in toluene. Standard atactic PS (\( M_w=178 \text{ kDa}, D(\text{polydispersity})=1.03, T_g=100^\circ\text{C} \), Polymer Standards Service—USA) was used to prepare several PS solutions in toluene (Rathburn Chemicals, \( \rho=0.867 \text{ g/cm}^3, T_b=110.6^\circ\text{C} \)). Toluene was chosen as solvent, as it is one of the most commonly used solvents for the spin-coating of PS films.

The films were spin-cast on fused quartz substrates. The substrates were first cleaned in an ultrasound bath, successively with acetone and ethanol, and then dried. To oxidize any impurities still present, the substrates were placed in chromosulphuric acid for at least 12 h, rinsed with double distilled water, dried in an oven at 120\(^\circ\text{C}\) for at least 2 h, and cooled in air until room temperature is reached.

To make films, toluene solutions of PS were filtered and spin-cast at 2,500 rpm for 30 s. The concentration of PS in the solution determines the thickness of the films obtained after spin-coating (which varied between 15 and 500 nm), as given by established master curves [30]. The agreement between the thickness of our films and the prediction of the master curves, as well as the uniformity of the films and the absence of defects, was checked by imaging with an atomic force microscope.

The films were prepared at room temperature. Spun films were placed in a flow of dry nitrogen, in a chamber with a temperature regulated at 115\(^\circ\text{C}\) (15\(^\circ\text{C}\) above the glass transition temperature of the polymer) for further drying and annealing, and then cooled down at room temperature. The films were dried for different times, ranging from 10 min to 6 h, to observe the kinetics of the desorption process.

Measurements techniques

To determine the amount of toluene retained in the films, we dissolved the annealed films with a good solvent (cyclohexanone) for both PS and toluene. The composition of the obtained mixture was then determined with GC. This technique has been already used to perform residual solvent analysis with bulk systems [31, 32]. The measurements were performed with a Carlo Erba GC 6000 Vega Series gas chromatographer, with a flame ionization detector coupled to a Hewlett-Packard HP3394A integrator. The injection temperature and the temperature of the column were 200\(^\circ\text{C}\); the temperature at the detector was 230\(^\circ\text{C}\).
Because the dependence of the signal given by the detector on the toluene quantity is not known, a calibration curve was made of the column response versus toluene concentration using solutions of toluene in cyclohexanone, with known concentrations in the range of 0.05–10 μl/ml. A fixed amount of acetonitril was also added as a reference to be able to correct for the differences in the quantities injected into the column of the gas chromatographer. The amount of toluene in the films was expected to be very small. To avoid systematic errors due to uncertainties on the baseline of the detector, we dissolved the films (which have a volume varying between 6 and 200 nl) with 50 μl of a toluene–cyclohexanone–acetonitrile solution with a known concentration of toluene. This ternary solution, called working solution, was beforehand analyzed with GC to use its toluene response as a reference. Then 2 μl of the solution resulting from the dissolution of the film was injected in the GC to determine the total concentration of toluene. This concentration had two contributions: (1) the toluene present in the working solution and (2) the toluene present in the dissolved film (which was always at least 10% of the first contribution). The difference between this last concentration and the concentration in the working solution gives then the amount of toluene present in the film. To obtain good statistics, the analysis of a given solution with GC was repeated three times, and for each film, parameters (thickness and drying time), about four films, were prepared and analyzed. The error bars given in the results show the standard deviation of the measurements.

With this measurement method, we reach detection limits of 10^{-2} μg/μl of toluene from the film in the working solution, which corresponds to a total mass of toluene in the films of 0.5 μg. We have checked the amounts of toluene measured with this method in the case of clean bare substrates (without any film) and bare substrates after spin-coating with pure toluene. The measured amounts of toluene were then zero within the measurement errors.

**Results and discussion**

From the GC measurements, we have obtained absolute values of the amount of toluene found inside the polymer films. We describe first the dependence of this amount on the film thickness (in the range 15–500 nm), after a drying time of 6 h, and in a second part the desorption kinetics.

**Thickness dependence**

The mass of toluene found in films is shown in Fig. 1a as a function of film thickness, for a drying time of 6 h at 115°C, which is 15°C above the glass transition temperature of the polymer. Note that all the films have the same area.

The results can also be translated in terms of the relative amount of solvent retained:

\[
M_r = \frac{M_T}{M_T + M_p}
\]

where \(M_T\) stands for the absolute amount of toluene retained in the film and \(M_p\) stands for the mass of polymer. \(M_p\) is defined as:

\[
M_p = \rho_p h_p A
\]

where \(\rho_p\) is the density of the pure polymer, \(h_p\) is the thickness of a film of pure polymer with mass \(M_p\), and \(A\) is the area of the substrate. The density \(\rho_p\) of the polymer can, in a very good approximation, be taken as its bulk value (\(\rho_p = 1,050\) kg m\(^{-3}\)). It is still a matter of debate whether or not the density of a polymer in an ultra-thin film is different from its density in bulk. For PS, most results agree, however, on the fact that the
polymer density in annealed films thicker than 10 nm is the same as in bulk [33, 34], and the density at the interface with air and with a supporting substrate differs from the bulk density over distances of at most a few nanometers [35–38].

The equivalent thickness \( h_P \) of pure polymer in the film can be obtained by subtracting from the film thickness \( h \) the thickness \( h_T \) of a layer of pure toluene of mass \( M_T \):

\[
h_P = h - h_T = h - \frac{M_T}{\rho_T} A
\]

where \( \rho_T \) is the density of toluene.

The results for the relative amounts \( M_r \) (Fig. 1b) show a significant increase as the film thickness decreases below 100 nm. For the thinnest films measured, the relative amount of toluene retained goes up to 35%. These ultra-thin samples were also observed under the optical microscope to look for a possible dewetting or breaking of the film, but no sign of it was found. This is consistent with reports in the literature that PS films with thicknesses above 2 nm are continuous [39, 40]. For film thicknesses above 200 nm, the relative amounts of solvent found in the films are of the order of a few percent or less.

The absolute amount of toluene retained in PS films has only a small dependence on the film thickness, which indicates that the solvent must be mainly located at the interfaces of the film. Another evidence for this segregation at interfaces is the expected glass transition temperature \( T_g \) of the films if the amount of toluene we find in the films was uniformly distributed in the films. For bulk PS, the dependence of \( T_g \) on the concentration of toluene absorbed in the polymer has been reported by Chow [41]. We can calculate what would be the glass transition temperature of the films assuming that the amount of toluene we find is uniformly distributed in the films. The result is plotted in Fig. 2, together with the glass transition temperature measured for supported PS films [26, 27], which are generally prepared by spin-coating from a toluene solution and subsequently dried above the glass transition. The values of \( T_g \) we find are well below the measured values, which agrees with our earlier conclusion that the toluene is concentrated at the interfaces.

It is most likely that the solvent is mainly located at the interface with the substrate rather than at the interface with air, as it would otherwise evaporate. As toluene is a good solvent for PS, there cannot be a sharp interface between the two, and full segregation is improbable. One should rather expect a significant increase of the toluene concentration at the interface with the substrate, which decreases over a certain length scale.

Segregation of solvent at the polymer/substrate interface of supported polymer films has already been observed in absorption experiments in which the films are put in the presence of the solvent vapor [21–25, 42]. It was attributed to the preferential interaction of the solvent with the substrate [25]. On the contrary, when this interaction is unfavorable, as in the case of water in the presence of a hydrophobic surface, a depletion of the solvent was observed close to the substrate [25].

To estimate the role of the molecule/substrate interactions in our case, we can evaluate the interfacial energies \( \gamma_{GT} \) and \( \gamma_{GP} \) of a glass/toluene and glass/PS interface, respectively, using the decomposition of interfacial energies in contributions corresponding to different interactions between the adjacent media [43, 44]. The interfacial energy \( \gamma_{12} \) between media 1 and 2 can be written in the following form:

\[
\gamma_{12} = \left( \sqrt{\gamma_{11}^{LW}} - \sqrt{\gamma_{22}^{LW}} \right)^2 + 2 \left( \sqrt{\gamma_{11}^+ \gamma_1^-} + \sqrt{\gamma_{22}^+ \gamma_2^-} - \sqrt{\gamma_{11}^+ \gamma_2^-} - \sqrt{\gamma_{12}^+ \gamma_{12}^-} \right)
\]

where \( \gamma_i^{LW} \) is the Lifschitz–van der Waals (or dispersive) component of the surface tension of medium \( i \), \( \gamma_i^+ \) is the electron-acceptor (Lewis acid) component, and \( \gamma_i^- \) is the electron-donor (Lewis base) component.
The fact that we evaluate $\gamma_{GT}$ and $\gamma_{GP}$ at room temperature instead of 115°C is not relevant, as the temperature dependence of the components are expected to significantly differ for toluene and PS [49, 50].

Using values of the different components available in the literature (Table 1), we obtain the following interfacial energies: $\gamma_{GT} = 12 \text{ mJ m}^{-2}$, $\gamma_{GP} = 11 \text{ mJ m}^{-2}$. These values are very close to each other, in particular in view of their variation on the method used to determine them. For instance, the interfacial energy of the glass/toluene interface can also be determined from the literature values of the surface tension of toluene ($\gamma_T = 29 \text{ mJ m}^{-2}$ [45, 46]), the contact angle of toluene on glass ($\theta = 68$° [46]), and the surface energy of glass ($\gamma_G = 48 \text{ mJ m}^{-2}$ [47]), using Young’s relation: $\gamma_{GT} = \gamma_G - \gamma_T \cos \theta = 19 \text{ mJ m}^{-2}$. This shows that the difference between the values of $\gamma_{GT}$ and $\gamma_{GP}$ found above is not significant and energetic considerations cannot explain the preferential location of toluene at the interface with the substrate.

Another factor determining the preferred location of solvent in our system is entropy. The presence of a hard wall reduces the number of configurations accessible to the polymer chains in the vicinity of the wall, reducing the entropy of the system. Concentrating small molecules at this interface decreases this effect and is therefore favorable with respect to a uniform distribution of solvent in the film. This is the same reason why chain ends are segregated at the interfaces of polymers [51–54].

Another interesting feature is the fact that the solvent retention shows a nontrivial behavior for thicknesses below 200 nm (Fig. 1a). This limit of 200 nm corresponds well to the thickness below, which the glass transition temperature of supported PS films departs from the bulk glass transition temperature [26, 27] (see also Fig. 2). This shows that this limit corresponds to the thickness below, which the behavior of the system departs from that in bulk. In the ‘bulk’ regime (thickness $> 200$ nm), the absolute amount of solvent retained is independent of film thickness, whereas in the thin-film regime (thickness $< 200$ nm), we find that the amount of solvent retained does depend on film thickness. It is however not clear what this dependence arises from.

### Table 1

| Material          | $\gamma_{LW}$ | $\gamma^+$ | $\gamma^-$ |
|-------------------|---------------|------------|------------|
| Glass [47]        | 37            | 1          | 45         |
| Toluene [45]      | 27            | 0          | 1          |
| Polystyrene [48]  | 36            | 0          | 1          |

The fact that we evaluate $\gamma_{GT}$ and $\gamma_{GP}$ at room temperature instead of 115°C is not relevant, as the temperature dependence of the components are expected to significantly differ for toluene and PS [49, 50].

Using values of the different components available in the literature (Table 1), we obtain the following interfacial energies: $\gamma_{GT} = 12 \text{ mJ m}^{-2}$, $\gamma_{GP} = 11 \text{ mJ m}^{-2}$. These values are very close to each other, in particular in view of their variation on the method used to determine them. For instance, the interfacial energy of the glass/toluene interface can also be determined from the literature values of the surface tension of toluene ($\gamma_T = 29 \text{ mJ m}^{-2}$ [45, 46]), the contact angle of toluene on glass ($\theta = 68$° [46]), and the surface energy of glass ($\gamma_G = 48 \text{ mJ m}^{-2}$ [47]), using Young’s relation: $\gamma_{GT} = \gamma_G - \gamma_T \cos \theta = 19 \text{ mJ m}^{-2}$. This shows that the difference between the values of $\gamma_{GT}$ and $\gamma_{GP}$ found above is not significant and energetic considerations cannot explain the preferential location of toluene at the interface with the substrate.

Another factor determining the preferred location of solvent in our system is entropy. The presence of a hard wall reduces the number of configurations accessible to the polymer chains in the vicinity of the wall, reducing the entropy of the system. Concentrating small molecules at this interface decreases this effect and is therefore favorable with respect to a uniform distribution of solvent in the film. This is the same reason why chain ends are segregated at the interfaces of polymers [51–54].

Another interesting feature is the fact that the solvent retention shows a nontrivial behavior for thicknesses below 200 nm (Fig. 1a). This limit of 200 nm corresponds well to the thickness below, which the glass transition temperature of supported PS films departs from the bulk glass transition temperature [26, 27] (see also Fig. 2). This shows that this limit corresponds to the thickness below, which the behavior of the system departs from that in bulk. In the ‘bulk’ regime (thickness $> 200$ nm), the absolute amount of solvent retained is independent of film thickness, whereas in the thin-film regime (thickness $< 200$ nm), we find that the amount of solvent retained does depend on film thickness. It is however not clear what this dependence arises from.

### Time dependence

We have also followed the amount of solvent retained over a time range from 0 to 6 h after the spin-coating. We observe a slight but systematic decrease of the mass of toluene in the films (Fig. 3). By fitting the data with a function of the form $M_0 \exp(-\alpha t)$, we can calculate the desorption rate $\alpha$. For a drying temperature of 115°C, this rate is in the range $1–5 \times 10^{-5}$ s$^{-1}$ for all film thicknesses (in the range 15–500 nm), with no clear thickness dependence. We have also performed the same measurements for a drying temperature of 25°C, and we find an desorption rate in the range $2–5 \times 10^{-6}$ s$^{-1}$. However, we reach with these measurements the limit of detectable mass differences, and this value should be considered an upper limit.

Our results at 115°C suggest that one should anneal the films for at least 16 h at this temperature to reduce the amount of solvent below the detection limit of 0.5 μg per film of our GC technique. The relative amount of solvent retained in the films would then vary from 0.3% for 500 nm-thick films to 9% for 15 nm-thick films. To reduce the concentration of toluene in these thinnest films to below 1%, one should anneal them for at least 43 h, but the absolute amounts of toluene present would then be so small that it would be very difficult to measure them.

The fact that the desorption rate is essentially independent of the film thickness is in agreement with results on absorption rates published in the literature. The absorption rate of water vapor in thin films of...
poly(vinyl pyrrolidone) [25] and in the polyelectrolyte poly(4-ammonium styrene sulfonic acid) [23] was also found to be independent of film thickness. Note, however, that we work in a rather different regime of solvent concentrations. The above mentioned polymers are hydrophilic, and the concentration of water in the films reaches 50% when they are put in the presence of saturated water vapor. In our case, the relative amount of solvent present is only a few percent for the thicker films.

To analyze their data, Vogt et al. [23, 25] assumed that the absorption rate was purely determined by the diffusion of the absorbed molecules, after the diffusion models developed for bulk and bulky films [55]. In this case, an absorption rate independent of film thickness means that $D/h^2$ (where $D$ is the diffusion coefficient of the absorbed molecules in the film) is independent of film thickness and, therefore, that $D$ varies as $h^2$ [23, 25]. If we make the same assumption, our observation also imply that the diffusion coefficient of toluene in the films varies as $h^2$ and, therefore, decreases by several orders of magnitude as the film thickness decreases down to ~10 nm. For the thickest films we have studied ($h = 500$ nm), the diffusion coefficient estimated from our measurements is $D \approx a h^2 \approx 5 \times 10^{-18}$ m$^2$s$^{-1}$, which can be considered as a lower limit for the bulk diffusion coefficient. This value is consistent with the extrapolation of bulk data obtained by Pickup and Blum [56] at the same temperature but for larger concentrations of toluene (11% and larger), which gives $D \approx 10^{-15} - 10^{-17}$ m$^2$s$^{-1}$.

There are several possible explanations for a decrease of the diffusion coefficient as film thickness decreases. Besides those already mentioned in the literature [25], a good candidate is the fact that polymer chains are aligned in the vicinity of interfaces. This has mainly been shown by computer simulations [52, 57–59], and a number of experimental results are consistent with such an interfacial alignment [60–62]. Such an alignment is expected to decrease the mobility of molecules in the direction perpendicular to the surfaces, while the mobility increases in the direction parallel. This has indeed been found in simulations for the mobility of the polymer itself [52]. Fluorescence recovery after photo-bleaching performed on thin PS films, which probes the in-plane diffusion, has shown that the diffusion coefficient of a dye increases (by up to two orders of magnitude) as the film thickness decreases [63, 64]. The alignment of polymer chains by rubbing has also been shown to decrease the diffusion of short chains out of the surface layer (i.e., the diffusion perpendicular to the surfaces decreases) but only by a factor 2 [65]. Our drying experiments, and the absorption experiments of Vogt et al. [23, 25], only probe the diffusion perpendicular to the film surfaces. In view of the above, we indeed expect that the diffusion coefficient determined from these experiments decreases when the film thickness decreases.

The fact that the desorption or absorption rate of small molecules in polymer films is independent of film thickness could, however, be interpreted in a different way than by changes in the diffusivity. This rate could be dominated by a process with a much longer characteristic time than the diffusion process. This is likely to happen for thin films, as the characteristic diffusion time through a film of thickness $h$ varies as $h^2$. Therefore, a process with a characteristic time much smaller than the diffusion time through a macroscopic sample (and therefore unnoticeable in the desorption/absorption dynamics of such systems), could become dominant for nanometric systems. In our experiments, the desorption of toluene from the polymer/substrate interface is a good candidate for such a rate-limiting process. At the present state of available data, it is not possible to distinguish between the two types of interpretation presented above.

**Conclusions**

GC is able to provide quantitative information on the absolute amount of solvent present in thin polymer films, for thicknesses down to ~10 nm. The thickness dependence of the absolute amount of toluene retained in PS films, after annealing and drying at 115°C, shows that the solvent is retained at the polymer/substrate interface. As the films get thinner, the relative amount of solvent increases significantly. The desorption rate is essentially independent of the film thickness. This could arise from a strong decrease of the diffusion coefficient of toluene in the polymer as film thickness decreases or from the fact that the desorption process is dominated by another process taking place at much longer time scales than the diffusion of the films.

**Acknowledgements** We thank the Softlink program of the Dutch Organization for Scientific Research (NWO), Akzo-Nobel and DSM for financial support. We thank D. Long for fruitful discussions.

**References**

1. Frank CW, Rao V, Despotopoulou MM, Pease RFW, Hinsberg WD, Miller RD, Rabolt JF (1996) Science 912: 912–915
2. Bornside DE, Macosko CW, Scriven LE (1987) J Imaging Sci Technol 13:122–130
3. Romdhane IH, Price PE, Miller CA, Benson PT, Wang S (2001) Ind Eng Chem Res 40:3065–3075
4. Richardson H, Sierrasnet M, Keddie JL (2003) Eur Phys J E 12:S87–S91
5. Brüel A, Boué F, Menelle A, Cotton JP (2000) Macromolecules 33:997–1001
6. Reiter G, de Gennes PG (2001) Eur Phys J E 6:25–28
7. Reiter G, Hamieh M, Damman P, Selavons S, Gabriele S, Vilmint T, Raphael E (2005) Nat Mater 4:754–758
8. Munda MK, Ellison CJ, Behling RE, Torkelson JM (2006) Polymer 47:7747–7759
9. Croll SG (1979) J Appl Polym Sci 23:847–858
10. Bornside DE, Macosko CW, Scriven LE (1989) J Appl Phys 66:5185–5193
11. Katz A, Ward MD (1996) J Appl Phys 80:4153–4163
12. Bouchard C, Guerrier B, Allain C, Laschitsch A, Saby AC, Johannsmann D (2000) J Appl Polym Sci 69:2235–2246
13. Guerrier B, Bouchard C, Allain C, Benard C (1998) Aiche J 44:791–798
14. de Gennes PG (2002) Eur Phys J E 7:31–34
15. Tsige M, Grest GS (2005) J Phys-Condens Matter 17:S4119–S4122
16. Saby-Dubreuil AC, Guerrier B, Allain C, Johannsmann D (1998) J Phys Chem Phys 110:10509–10513
17. Pan L, Zhang M, Nakayama Y (1999) J Chem Phys 110:20509–20513
18. Bistac S, Schultz J (1997) Prog Org Coat 31:347–350
19. Grohens Y, Hamon L, Spevacek J, Holl Y (2003) Macromol Symp 203:155–162
20. To T, Wang H, Djurisic AB, Xi M, Chan WK, Xie Z, Wu C, Tong SY (2004) Thin Solid Films 46:59–65
21. Wu WL, Orts WJ, Majkrzak CJ, Hunston DL (1995) Polym Eng Sci 35:1000–1004
22. Tan NCB, Wu WL, Wallace WE, Davis GT (1998) J Polym Sci B 36:155–162
23. Vogt BD, Soles CL, Lee HJ, Lin EK, Wu WL (2004) Langmuir 20:4135–4145
24. Vogt BD, Soles CL, Jones RL, Wang CY, Lin EK, Wu WL, Satija SK, Goldfarb DL, Angelopoulos M (2004) Langmuir 20:5285–5290
25. Vogt BD, Soles CL, Lee HJ, Lin EK, Wu WL (2005) Polym Sci B 43:1635–1642
26. Forrest JA, Dalnoki-Veress K (2001) Adv Colloid Interface Sci 94:167–196
27. Forrest JA, Jones RAL (2000) The glass transition and relaxation dynamics in thin polymer films. In: Karim A, Kumar S (eds) Polymer surfaces, interfaces and thin films. World Scientific, Singapore, pp 251–294
28. Alcoutlabi M, McKenna GB (2005) J Phys Condens Matter 17:R461–R524
29. Reiter G, Forrest JA (eds) (2002) Special issue on properties of thin polymer films, vol 8 of Eur Phys. J. E, pp 101–266
30. Shapovalov V, Zaitov VS, Strzhemenech Y, Choudhery F, Zhao W, Schwarz SA, Ge S, Shin K, Sokolov J, Rafailovich MH (2000) Polym Int 49:432–436
31. Kumar N, Gov J (1994) J Chromatogr A 235:235–240
32. Uraikami K, Saito Y, Fujiwara Y, Watanabe C, Umemotok K, Godo M, Hashimoto K (2000) Chem Pharm Bull 48: 1894–1897
33. Wallace WE, Tan NCB, Wu WL, Satija S (1998) J Chem Phys 108:3798–3804
34. Reiter G (1994) Macromolecules 27:3046–3052
35. Xie L, DeMaggio GB, Frieze WE, Devries J, Gildey DW, Hristov HA, Yee AF (1995) Phys Rev Lett 74:4947–4950
36. Bollinne C, Stone VW, Carlier V, Jonas AM (1999) Macromolecules 32:4719–4724
37. Cao H, Yuan JP, Zhang R, Sundar CS, Jean YC, Suzuki R, Ohdaira T, Nielsen B (1999) Appl Surf Sci 149:116–124
38. Algers J, Suzuki R, Ohdaira T, Maurer FHJ (2004) Polymer 45:4533–4539
39. Stange TG, Mathew R, Evans DF, Hendrickson WA (1992) Langmuir 8:920–926
40. Extrand CW (1993) Langmuir 9:475–480
41. Chow TS (1980) Macromolecules 13:362–364
42. Kent MS, Smith GS, Baker SM, Nyitray A, Browning J, Moore G, Hua DW (1996) J Mater Sci 31:927–937
43. Fowkes FM (1962) J Phys Chem 66:5185–5193
44. Van Oss CJ, Chaudhury MK, Good RJ (1988) Chem Rev 88:927–941
45. Jaiczuk B, Bialopiotrowicz T (1989) J Colloid Interface Sci 127:189–204
46. Gunde R, Hartland S, Mader R (1995) J Colloid Interface Sci 176:17–30
47. Radelczuk H, Holysz L, Chibowski E (2002) J Adhes Sci Technol 16:1547–1568
48. Peters RD, Yang XM, Kim TK, Sohn BH, Nealey PF (2000) Langmuir 16:4625–4631
49. Wu W (1970) J Phys Chem 74:632–638
50. Fröba AP, Leipertz A (2001) Int J Thermophys 22:41–59
51. Kumar SK, Vacatello M, Yoon DY (1988) J Chem Phys 89:5206–5215
52. Bitsanis I, Hadziioannou G (1990) J Phys Chem 92:3827–3847
53. Tanaka K, Taura A, Ge SR, Takahara A, Kajiyma T (1996) Macromolecules 29:3040–3042
54. Kajiyma T, Tanaka K, Takahara A (1997) Macromolecules 30:280–285
55. Crane K (1975) The mathematics of diffusion, 2nd edn. Oxford Univ. Press, Oxford
56. Pickup S, Blum FD (1989) Macromolecules 22:3961–3968
57. Kumar SK, Vacatello M, Yoon DY (1990) Macromolecules 23:2189–2197
58. Baschnagel J, Binder K (1995) Macromolecules 28:6809–6818
59. Mischler C, Baschnagel J, Binder K (2001) Adv Colloid Interface Sci 94:197–227
60. Jones RL, Kumar SK, Ho DL, Blue RG, Russell TP (1999) Nature 386:146–149
61. Jones RL, Kumar SK, Ho DL, Blue RG, Russell TP (2001) Macromolecules 34:559–567
62. Briggs KA, Stephenson JC, Wallace WE, Richter (2001) J Phys Chem B 105:2785–2791
63. Tseng KC, Turro NJ, Durning CJ (2000) Phys Rev E 61:1800–1811
64. Tseng KC, Turro NJ, Durning CJ (2000) Polymer 41:4751–4755
65. Pu Y, White H, Rafailovich MH, Sokolov J, Schwarz SA, Dhinojwala A, Agra DMG, Kumar S (2001) Macromolecules 34:4972–4977