Thermal Characterization of PMMA Thin Films Using Modulated Differential Scanning Calorimetry

Crystal E. Porter and Frank D. Blum*

Department of Chemistry and Materials Research Center, University of Missouri—Rolla, Rolla, Missouri 65409

Received February 17, 2000; Revised Manuscript Received July 14, 2000

ABSTRACT: Modulated differential scanning calorimetry was used to probe the thermal behavior of poly(methyl methacrylate) (PMMA) adsorbed onto silica from solution and subsequently dried. Changes in the glass transition were studied as a function of the adsorbed amount and solvent system used to deposit the polymer. The glass transition temperature (T_g) of PMMA was found to increase from 108 °C for the bulk polymer to 136 °C for the polymer adsorbed on silica from toluene ($1.0A_m$). For the polymer adsorbed at approximately half that amount ($0.6A_m$), the glass transition temperature increased to 158 °C. The breadth of the transition also increased from 11 °C for bulk to 61 and 58 °C for the $1.0A_m$ and $0.6A_m$ samples, respectively. When PMMA was adsorbed from a mixed solvent system (5:1 benzene/acetonitrile solution), the transition temperature and its breadth increased even further. For a sample with $0.5A_m$ adsorbed amount from the mixed solvent system, the T_g was increased to 167 °C and the width of the transition was increased to 65 °C. The change in thermal behavior was attributed to polymer chain confinement, resulting in a distribution of segmental mobilities different from that of the bulk polymer. Upon aging for 328 days from the original analysis date, the polymer chains in the $0.6A_m$ sample adsorbed from toluene rearranged, resulting in thermal behavior which was more like that of the $0.5A_m$ sample adsorbed from the mixed solvent system.

Introduction

The number of studies of thin polymer films has increased in recent years,[1−15] and their findings have taken on more significance as technological devices incorporate the use of thin polymer-containing films. An understanding of the interaction between the polymer and substrate is especially needed as the thicknesses of the films approach molecular dimensions. In polymer-coated materials, thin layers may constitute only a small volume or weight fraction of the system studied, but they may have a significant impact on the behavior of the system.[16] Very sensitive instrumentation is needed for characterization of such small components.

Some techniques used to examine bound-polymer behavior are sensitive to segmental dynamics (or molecular motion) in the film such as electron spin resonance (ESR),[1,2,17,18] nuclear magnetic resonance (NMR),[3,4] and dielectric measurements.[9] Other techniques are used to relate the local structure or thickness changes in the polymer layer, such as positron lifetime spectroscopy,[5,6] spectroscopic ellipsometry,[7,8] X-ray,[10,11] and neutron[12,13] reflectometry. Even though various studies have attempted to characterize polymer thin films, the effects resulting from the interactions between the polymer and the substrate are still not sufficiently understood.

The above studies showed that polymer/substrate interactions and film thicknesses could significantly change the characteristics of polymer films. It may be that, in addition to the different polymer/substrate interactions, the different experiments themselves may be sensitive to different attributes of the polymer/substrate system. Although several techniques have been used to study these films, uncertainty still remains about how adsorbed amounts influence polymer mobility. Therefore, it is valuable to conduct additional studies and explore other methods for determining the onset of large-scale segmental motion (which we use as our working definition of the glass transition temperature).

Differential scanning calorimetry (DSC) is the most widely used method for studying the T_g of bulk polymer systems.[19] Until recently, typical laboratory instrumentation was not sensitive enough to adequately resolve the thermal transitions of very thin films. Temperature-modulated DSC (MDSC) is a modified version of regular DSC which uses an oscillatory heating ramp that results in increased instantaneous heating rates.[19,20] This change in heating rates, combined with other enhancements, can increase the instrument's sensitivity so that it can be used to characterize very thin films.

This paper reports the use of modulated differential scanning calorimetry to examine the glass transition behavior of poly(methyl methacrylate) adsorbed on silica. We varied the amount of polymer adsorbed, as well as the solvent from which the polymer was adsorbed, and found that the glass transition region increased with decreased coverage. To our knowledge, this is the first reported analysis of such very thin polymer films using DSC.

Experimental Section

Adsorption. Atactic PMMA was obtained from Aldrich Chemical, Milwaukee, WI. From ^{13}C and ^{1}H NMR analysis,[21] the polymer was estimated to have 50% rr, 40% mr, and 10% mm triads. The M_w was 90 kg/mol, and the polydispersity was 1.5, as measured in our laboratory using gel permeation chromatography in tetrahydrofuran. PMMA solutions of various concentrations were prepared using either toluene or a 5:1 benzene/acetonitrile (v/v) solvent system. After dissolution, the solutions were allowed to equilibrate with known quanti-

---

* To whom correspondence should be sent.

10.1021/ma000302l CCC: $19.00

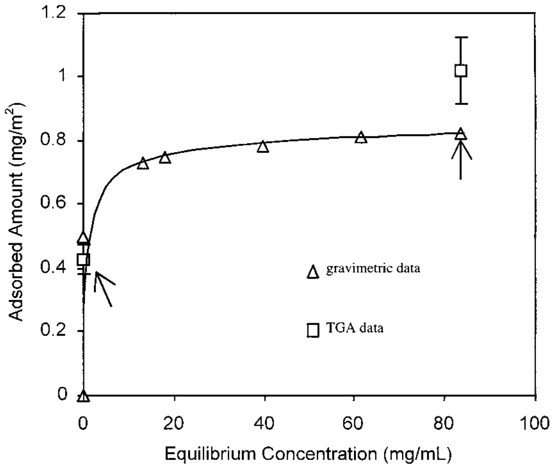

Figure 1. Adsorption isotherm for PMMA (M_w = 90 kg/mol, PD = 1.5) adsorbed onto silica from toluene and dried. The arrows indicate the samples from this solvent system which were analyzed with MDSC and reported in this study.

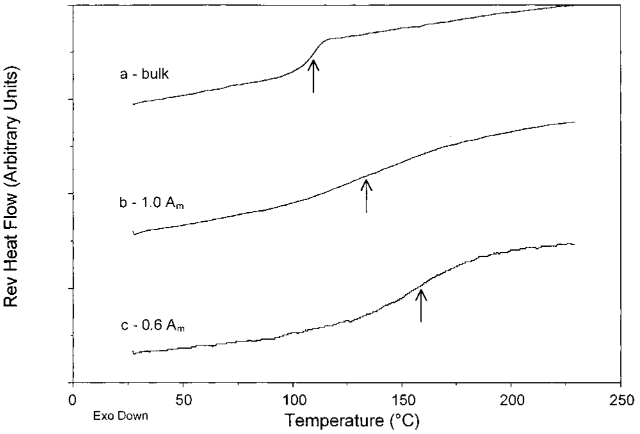

Figure 2. MDSC thermograms (rate = 2.5 °C/min, amplitude = ±1 °C, period = 60 s) of PMMA in bulk and adsorbed onto silica. Thermograms are from (a) bulk PMMA, (b) 1.0A_m, and (c) 0.6A_m coverage. The arrows show estimates of the center of the transitions. The positions on the vertical axis are shifted to distinguish between the different curves.

ties of amorphous fumed silica (M-5 grade, Cabot Corp., Tuscola, IL) which was heat-treated at 400 °C for at least 12 h. The nonporous silica had a surface area of 200 m^2/g. The samples were shaken in a mechanical shaker for 48 h at 22 °C. Initial and steady-state solution concentrations were determined gravimetrically after drying a known volume of the supernatant solution. The adsorbed amounts were calculated from the changes in the concentration before and after adsorption. The adsorbed amounts of polymer in several samples, which were checked, were close to those measured using thermal gravimetric analysis, with an experimental error of 7% or less. The treated silica was centrifuged and rinsed three times with the appropriate solvent system to remove any excess polymer (beyond a monolayer in the dispersion) present. The PMMA/silica samples were then dried under vacuum at 70 °C for 12 h and stored in a desiccator until used.

Characterization. A TA Instruments model 2920 MDSC (New Castle, DE) was used to thermally analyze the coated silica samples. The reference pan was loaded with roughly the equivalent amount of silica as was in the sample pan to emphasize the thermal behavior of the adsorbed polymer. The heat flow curves were normalized to the mass of the polymer only and not to the mass of the total sample. Two heating scans and one cooling scan were taken from 25 to 240 °C, at a rate of 2.5 °C/min, a modulation amplitude of ±1 °C, and a period of 60 s. The total run time per sample was approximately 4 h. The mass of the sample was approximately 7−8 mg, and the cell was purged with nitrogen gas at 50 mL/min during the scans.

The second heating scan was used to determine the glass transition data from the reversing heat flow curves so that all of the samples were subjected to a similar thermal history. The reported T_g was found by using the half-height temperature of the transition step. T_g values from at least two separate experiments were averaged for the bulk and all surface samples. A difference of no more than ±2 °C was observed for experiments performed on different samples of the same material. The thermograms shown in the figures were purposely shifted vertically on the heat flow axis to aid in comparing the transitions of the different samples. The behaviors of the samples in the plateau region were basically independent of the sample studied.

Results and Discussion

Coverage Effects. Figure 1 shows the adsorption isotherm from gravimetric data for PMMA adsorbed onto silica from toluene. The plateau region revealed that the maximum adsorbed amount (defined as 1.0A_m coverage) was approximately 0.80 mg/m^2. This value was comparable to those found in other PMMA adsorption studies that used thermodynamically poor solvents. In these studies, the maximum adsorption amounts ranged from 0.6 to 1.5 mg/m^2.[17,22−25] The adsorption at lower coverages was reported relative to this maximum amount (1.0A_m) using the isotherm values. Data points from TGA experiments that corresponded to the samples that were subjected to thermal analysis were also included in the isotherm. On the basis of the difference between the isotherm values and the TGA data, we estimated the error for the different coverages to be roughly ±0.1A_m. An adsorption isotherm was not measured for the mixed-solvent system. For this system, concentrations believed to yield plateau coverages were used to prepare the adsorbed samples.

The thermograms for PMMA in bulk and on silica (1.0A_m and 0.6A_m) are shown in Figure 2. The glass transition temperature for bulk PMMA was about 108 °C, and the T_g span from the onset to the end was about 11 °C. These values are close to the accepted values[19] for atactic PMMA using the standardized heating rate of 10 °C/min (105 and 10 °C for the transition's midpoint and breadth, respectively).

The T_g for the adsorbed polymer, approximately 136 °C at saturation coverage in toluene (1.0A_m), was higher than that of bulk. The temperature span associated with the transition broadened significantly to about 61 °C for the 1.0A_m sample (Figure 2). The glass transition temperature increase for the 0.6A_m coverage was even higher, at about 158 °C, and had roughly the same span as the 1.0A_m sample (approximately 58 °C). These results are summarized in Table 1.

Polymer composites,[26−28] polymer blends,[29,30] and interpenetrating polymer networks[31] have also been known to show trends similar to that reported here in the glass transition behavior when compared to bulk. Pallikari-Viras et al.[26] have shown a broader and increased T_g in PMMA/gel silica glass composites using regular DSC. They reported a T_g span of 35 °C for bulk that increased to 60 °C for the composite which was centered 60 °C higher than bulk. Dynamic mechanical studies by Tsagaropoulos and Eisenberg[28] found that various filled polymers exhibited a second thermal transition peak for polymer regions that were reduced in mobility. These glass transitions were found at higher temperatures and were broader than their correspond-

Table 1. Glass Transition Data (in °C)for Bulk and Surface-Adsorbed PMMA

sample	glass transition temp[a]	transition onset temp	transition end temp	width of transition
bulk	108	103	114	11
$1.0A_m$[b]	136	106	167	61
$0.6A_m$[b]	158	129	187	58
$0.5A_m$[c]	167	134	199	65
$0.6A_m$[d]	164	138	190	52

[a] Defined as the temperature associated with the half-height of the transition. [b] Adsorbed from toluene, $1.0A_m$ corresponds to 0.80 mg/m^2. [c] Adsorbed from 5:1 benzene/acetonitrile solution. [d] Aged sample from toluene (328 days from original analysis date).

ing bulk values. In these studies no attempt was made to focus on the behavior of the initial (primary contact) layer.

While the above studies did not focus on a molecularly thin film, other spectroscopic studies have. Keddie et al.[7] used ellipsometry to study PMMA spin-coated onto native oxide silicon and found that T_g increased slightly as the thickness decreased. Grohens et al.[8] also used ellipsometric techniques to analyze glass transition differences of stereospecific PMMA films on silicon and aluminum. For both surfaces they found that thin films of isotactic and atactic PMMA have a higher T_g compared to bulk whereas syndiotactic PMMA films have a lower T_g. Wu et al.[12,13] using neutron reflectivity found a more pronounced increase in the T_g of PMMA on silica. While they attempted to interpret their data in terms of a two-state model, they speculated that a broader distribution might be possible. All of these authors attributed their findings to strong interfacial interactions. The increase in glass transition temperature we found was consistent with those studies cited above, but the magnitude of the increases in T_g and its breadth were much greater in our study. This difference may be due to the following reasons: (i) A recent study by Kahle et al.[32] showed that the index of refraction of silicon is temperature dependent. Inclusion of the temperature-dependent index may somewhat alter the values T_g estimated from ellipsometry. (ii) In the ellipsometry and neutron analysis, a linear relationship between the measured thickness and temperature was assumed before and after T_g. The T_g values were basically determined by the *intersection* of two lines. Our MDSC data clearly show that the heat capacity changes over a broad range of temperatures, which, we believe, result from a distribution in segmental mobility. This effect should also be present in the ellipsometry data, but it may be masked because of the inflection and uncertainty in the ellipsometry data. Presently, it is unclear whether the inflection point measured by ellipsometry correlates with the onset of large-scale segmental motion for some portion of the sample or the whole sample.

When a homopolymer is adsorbed onto a substrate, it is expected to assume a configuration that is composed of trains, loops, and tails.[33] The trains are the segments that are in direct contact with the surface. Loops and tails are comprised of segments, which dangle away from the surface. Two trains terminate the loops, whereas the tails are bound only at one end. Taking the configuration of the polymer and a limited number of surface sites into account, the relative number of trains would be expected to decrease with increased adsorbed amounts. At lower surface coverages, the polymer would be expected to take on a flatter configuration because of the increased relative number of contacts.

As a glassy polymer becomes rubbery, the onset of longer-range segmental motions becomes evident. For adsorbed polymers that are attracted to the surface (such as PMMA/silica), those segments closer to the surface are anchored and have less mobility compared to those further away. For PMMA on silica, we expect that the onset temperature was indicative of the onset of long-range motions for the regions in the film that were least restricted (i.e., loops and tails). The end temperature would be indicative of the more restricted regions (trains or segments near the trains), requiring increased thermal energy to become mobile.

Previous studies have shown that the glass transition temperature can increase and broaden due to polymer chain confinement that results from intermolecular interactions,[27,34] in particular, hydrogen bonding.[35,36] Since it is known that the adsorption mechanism for PMMA on silica is through hydrogen bonding,[26,36,37] it is reasonable that the T_g elevation was the result of segmental restrictions due to some of the segments being bound to silica. Flatter configurations from lower adsorbed amount samples[14] had fractionally more restrictions and a higher T_g.

Our findings are also consistent with previous studies using deuterium NMR on poly(methyl acrylate) (PMA) on silica. Lin and Blum[4] found that a distribution of mobilities existed in the adsorbed polymer layer. At all of their surface coverages, a small amount of material with *enhanced* mobility was observed with an onset temperature of approximately 5 °C below the bulk NMR T_g. The majority of the polymer segments had mobilities that were more restricted or slower than those of bulk. At a temperature of about 30 °C above the bulk T_g, fewer than 10% of the polymer segments were estimated to be rigid on the deuterium NMR time scale. Lin and Blum proposed that the lower temperature onset was due to polymer segments near the polymer−air interface. The more restricted segments were assigned as those segments closer to the polymer−silica interface. In other words, the interface was graded in terms of mobility. Since PMA and PMMA should have similar affinities for silica through hydrogen bonding, it is reasonable to believe that a graded interface exists in our PMMA films as well. Since the amount of highly mobile species would be expected to be small, it is likely that our MDSC was not sensitive enough to detect these segments. Thus, primarily what we observed was the restricted mobility of the rest of the chain segments.

Solvent Effects. Figure 3 shows the thermograms of $0.6A_m$ and $0.5A_m$ samples of PMMA on silica that were adsorbed from toluene and benzene/acetonitrile solvents, respectively. The polymer adsorbed from toluene had a glass transition of about 158 °C with a span of roughly 58 °C while the sample adsorbed from the mixed solvent system had a T_g of around 167 °C and a span of approximately 65 °C.

The decrease in the maximum amount of PMMA adsorbed using the cosolvent system resulted from the interactions between the polymer, solvent, and substrate. The most significant effect was likely due to an increase in solvent polarity. Though we have not made detailed studies on the effects of cosolvent systems, it seems likely that the increased polarity made the solvent thermodynamically better for PMMA than toluene. This may have resulted in an increase the polymer coil size in solution, and, ultimately, a more extended configuration of the chain at the surface. Then, upon

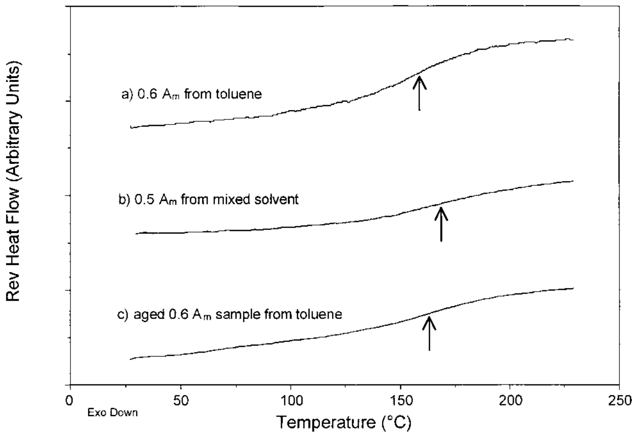

Figure 3. MDSC thermograms (rate = 2.5 °C/min, amplitude = ±1 °C, period = 60 s) of $0.6A_m$ and $0.5A_m$ coverages of PMMA adsorbed onto silica and dried which were adsorbed from toluene and the mixed solvent system, respectively. (a) Adsorbed from toluene, (b) adsorbed from a 5:1 benzene/acetonitrile solution, and (c) aged sample adsorbed from toluene. The arrows are estimates of the center of the transitions. Their positions on the vertical axis are shifted to distinguish between the different curves.

drying from the mixed-solvent system, an even flatter configuration might be expected. We believe that the increased number of segmental contacts resulting from the more flattened conformation restricted the mobility of the polymer further and, thus, shifted the T_g to an even higher temperature with slightly more broadening.

Aging Effects. The thermal behavior of the treated samples was investigated after they had been aged at 22 °C. The period of aging was 328 and 231 days for the toluene-cast and mixed solvent-cast samples, respectively, and 336 days for the $1.0A_m$ sample from toluene. The thermograms for the $0.5A_m$ sample from the mixed-solvent system and the $1.0A_m$ sample from toluene did not differ significantly from the earlier runs and therefore are not shown. However, after aging, the thermal behavior of the $0.6A_m$ toluene-cast sample became more like that of the mixed-solvent sample (see Figure 3). The T_g of the sample from toluene increased from 148 to 164 °C, and the transition's onset and end point increased from 129 to 138 °C and from 187 to 190 °C, respectively.

Because of the inherent instability of the glassy state, over time, the physical nature of polymers below their T_g gradually change toward equilibrium.[38] In thin films, the nonequilibrium state of the polymer at the polymer/substrate interface is also known to contribute to unstable configurations.[39] It is therefore not surprising that we observed a change in the thermal behavior during prolonged times when the polymer chains rearranged themselves to, presumably, more stable configurations. The significant increase in the transition's onset implies that the major effect was the reduction of mobility of the polymer segments at the polymer/air interface. The only slight increase in the end temperature suggests that the nature of the segments at the polymer/substrate interface (trains) were not changed much with time. However, the relative number of more restricted segments increased with time. Thus, it appears that more segments in the $0.6A_m$ toluene-cast sample may have attached themselves to the surface with age.

Blum et al.[40] used AFM to show that a saturation coverage of PMMA on a silicon wafer did not uniformly cover the surface when adsorbed from toluene. PMMA's structure appeared to have aggregates of polymer in some regions of the surface and other regions where the polymer did not attach. It is likely that similar structures would exist on a silica surface. Since our $0.6A_m$ sample from toluene would also have these open regions of unoccupied surface, it is plausible that the polymer segments rearranged to more stable configurations, increasing the number of trains. The unchanged behavior of the mixed-solvent-cast sample and the change in the 0.6 sample from toluene leads us to believe that the more extended polymer configuration, with more segments in trains, was more stable than the original configuration from toluene.

Heating a polymer sample above T_g can often restore the preaged state of bulk polymer systems;[36] however, the behavior of all of our aged samples did not change significantly upon further heating. We note that there seemed to be a slight increase in T_g with an increased time of annealing when our earlier-tested toluene-cast sample was heated to 240 °C for 24 h. However, the significance of this trend is questionable since the T_g values were within our experimental error (not shown). In any event, the rearrangement of the polymer segments to their "relaxed" state must be a slow process, even at elevated temperatures.

Conclusions

We have reported the use of MDSC to characterize thin films and have shown that the thermal behavior of these films of poly(methyl methacrylate) on silica varied as a function of the adsorbed amount and the solvent used. The glass transition temperatures of the $1.0A_m$ and $0.6A_m$ coverages from toluene increased from 108 to 136 and 158 °C, respectively, compared to that of bulk. The breadth of the transitions also increased from 11 °C for bulk to 61 and 58 °C for $1.0A_m$ and $0.6A_m$ coverages from toluene, respectively. The $0.5A_m$ coverage from a thermodynamically better solvent system also showed a T_g increase to 167 °C with a span of 65 °C. We suggest that the increase and broadening in T_g resulted from segmental confinement of the attached polymer. In addition, we believe that the increased T_g results from a broad distribution of polymer mobility that is consistent with earlier spectroscopic studies.

An aging effect was also observed for the $0.6A_m$ sample from toluene. When the sample was aged for 328 days from the original date of analysis, the T_g increased to 164 °C and its breadth changed to 52 °C. At long times, it seems as though the polymer chains rearranged themselves into more stable configurations with more segments in trains. These aging results were consistent with the lower coverage sample adsorbed from the mixed solvent system having a more extended configuration compared to those adsorbed from toluene. In addition, the $0.6A_m$ adsorbed amount sample from toluene appeared to have more extended configurations than the $1.0A_m$ sample. In other words, there were higher fractions of segments in trains than the larger adsorbed amount sample.

Acknowledgment. The authors acknowledge the support of the National Science Foundation under Grant DMR 9807696. The authors thank Dr. H. Jo for his help in determining the tacticity of the polymer on short notice.

References and Notes

(1) Thambo, G.; Miller, W. G. *Macromolecules* **1990**, *23*, 4397.
(2) Liang, T. M.; Dickenson, P. N.; Miller, W. G. In *Polymer Characterisation by ESR and NMR*; Woodward, A. E., Bovey, F. A., Eds.; American Chemical Society: Washington, DC, 1980; Chapter 1.
(3) Blum, F. D. *Annu. Rep. NMR Spectrosc.* **1994**, *28*, 277.
(4) Lin, W. Y.; Blum, F. D. *Macromolecules* **1997**, *18*, 5331; **1998**, *31*, 4135.
(5) DeMaggio, G. B.; Frieze, W. E.; Gidley, D. W.; Zhu, M.; Hristov, H. A.; Yee, A. F. *Phys. Rev. Lett.* **1997**, *78*, 1524.
(6) Jean, Y. C.; Zhang, R. W.; Cao, H.; Yuan, J. P.; Huang, C. M.; Nielsen, B.; Asoka-Kumar, P. *Phys. Rev. B* **1997**, *56*, R8459.
(7) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Europhys. Lett.* **1994**, *27*, 59; *Faraday Discuss.* **1994**, *98*, 219.
(8) Grohens, Y.; Brogly, M.; Labbe, C.; David, M.; Schultz, J. *Langmuir* **1998**, *14*, 2929.
(9) Hodge, T. C.; Bidstrup, S. A.; Kohl, P. A. *J. Polym. Sci., Polym. Phys. Ed.* **1999,** *37*, 311.
(10) Orts, W. J.; van Zanten, J. H.; Wu, W.; Satija, S. K. *Phys. Rev. Lett.* **1993**, *71*, 867.
(11) Reiter, G. *Macromolecules* **1994**, *27*, 3046; *Europhys. Lett.* **1993**, *23*, 579.
(12) Wu, W.-L.; Orts, W. J.; van Zanten, J. H.; Fanconi, B. M. *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1994**, *32*, 2475.
(13) Wu, W.-L.; van Zanten, J. H.; Orts, W. J. *Macromolecules* **1995**, *28*, 771.
(14) Douglas, H. F.; Schneider, H. M.; Frantz, P.; Lipman, R.; Granick, S. *J. Phys.: Condens. Matter* **1997**, *9*, 7699.
(15) Johnson, H. E.; Granick, S. *Macromolecules* **1990**, *23*, 3367.
(16) Wool, W. P. *Polymer Interfaces Structure and Strength*; Hanser/Gardner: Cincinnati, OH, 1995; Chapter 1.
(17) Sakai, H.; Fujimori, T.; Imamuri, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3457.
(18) Hommel, H. *Adv. Colloid Interface Sci.* **1995**, *54*, 209.
(19) Turi, E. A. *Thermal Characterization of Polymeric Materials*, 2nd ed.; Academic Press: San Diego, CA, 1997; Vol. 1.
(20) Sauerbrunn, S. R.; Crowe, B. S.; Reading, M. *Polym. Mater. Sci. Eng.* **1993**, *68*, 269.
(21) Ferguson, R. C.; Ovenall, D. W. *Polym. Prepr.* **1985**, *26* (1), 182.
(22) Ellerstein, S.; Ullman, R. *J. Polym. Sci.* **1961**, *55*, 123.
(23) Thies, C. *J. Polym. Sci., Part C* **1971**, *34*, 201.
(24) Kobayashi, K.; Araki, K.; Imamuri, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3421.
(25) Kobayashi, K.; Sugimoto, S.; Yajima, H.; Araki, K.; Imamura, Y.; Endo, R. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2018.
(26) Pallikari-Varas, F.; Li, X.; King, T. A. *J. Sol.-Gel Sci. Technol.* **1996**, *7*, 203.
(27) Çaykara, T.; Güven, O. *J. Appl. Polym. Sci.* **1998**, *70*, 891.
(28) Tsagaropoulos, G.; Eisenberg, A. *Macromolecules* **1995**, *28*, 6067.
(29) Song, M.; Hammiche, A.; Pollock, H. M.; Hourston, D. J.; Reading, M. *Polymer* **1996**, *37*, 5661.
(30) Song, M.; Hourston, D. J.; Pollock, H. M.; Hammiche, A. *Polymer* **1999**, *40*, 4763.
(31) Hourston, D. J.; Song, M.; Schafer, F. U.; Pollock, H. M.; Hammiche, A. *Polymer* **1999**, *40*, 4769.
(32) Kahle, O.; Wielsch, U.; Metzner, H.; Bauer, J.; Uhlig, C.; Zawatzki, C. *Thin Solid Films* **1998**, *313*, 803.
(33) Fleer, G. J.; Cohen-Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T. Vincent, B. *Polymers at Interfaces*; Chapman & Hall: London, 1993.
(34) Vaia, R. A.; Sauer, B. B.; Tse, O. K.; Giannelis, E. P. *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1997**, *35*, 59.
(35) Hatekeyama, T.; Hatakeyama, H. *Thermochim. Acta* **1995**, *267*, 249.
(36) Chehimi, M. M.; Watts, J. F. *J. Electron Spectrosc. Relat. Phenom.* **1993**, *63*, 393.
(37) Allara, D. L.; Wang, Z.; Pantano, C. G. *J. Non-Cryst. Solids* **1990**, *120*, 93.
(38) Struik, L. C. E. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Kroschwitz, J. I., Ed.; Wiley: New York, 1985; Vol. 1, p 595.
(39) Bluestein, S. D.; Bramono, D. P. Y.; Miaoulis, I. N.; Wong, P. Y. *Mater. Res. Soc. Symp. Proc.* **1997**, *445*, 185.
(40) Blum, F. D.; Sparr, E., submitted for publication.

MA000302L