

POLYSTYRENE THIN FILMS WITH INCORPORATED BORANE CLUSTERS FOR ELECTRONIC APPLICATIONS INVESTIGATED BY INFRARED REFLECTION-ABSORPTION SPECTROSCOPY

Barbora HANULIKOVA, Tereza CAPKOVA, Jan ANTOS, Jakub SEVCIK, Pavel URBANEK, Michal URBANEK, Ivo KURITKA

Tomas Bata University in Zlín, University Institute, Centre of Polymer Systems, Zlín, Czech Republic, EU, hanulikova@utb.cz

<https://doi.org/10.37904/nanocon.2020.3699>

Abstract

The paper is focused on the investigation of thin polystyrene (PS) films and PS films with incorporated *anti*-octadecaborane(22) (*anti*-B₁₈H₂₂) clusters (PS+B₁₈H₂₂) with a thickness of 450 nm and 290 nm, respectively. The main aim is to describe the vibrational behavior of thin films in dependence on temperature and determine the changes connected with the glass transition of PS. Infrared reflection-absorption spectra were measured and from the plot of spectral region area (A_{range}) vs. temperature, glass transition temperature (T_g) of PS was extracted. The abrupt change in the course of A of C_{ar}-H stretching vs. temperature was assigned to the glass transition. T_g of PS and PS+B₁₈H₂₂ thin film was determined to be 74 °C and 77 °C, respectively. On the other hand, only a continuous decrease of A of C-H stretching vs. temperature was found for both samples indicating that each vibrational motion reacts uniquely on temperature increase. It was further found that *anti*-B₁₈H₂₂ is not fixed firmly in the thin layer at higher temperatures, because no B-H spectral response was detected above 91 °C. This result was also supported with TGA and DSC analysis showing a particular mass decrease at temperature 75 °C.

Keywords: Octadecaborane, polymer blend, thin film, glass transition, infrared reflection-absorption spectroscopy

1. INTRODUCTION

Polymer thin films have attracted attention due to their specific properties related to the thin layer arrangement of macromolecules. Semi-conductive polymer layers (e.g. MEH-PPV, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]) have found their use in light-emitting diodes preparation [1] and insulating polymer layers (PS, polystyrene or PMMA, poly[(methyl) methacrylate] etc.) have been used as matrices for the incorporation of low molecular species. For example, blue-emitting borane clusters, especially *anti*-octadecaborane(22) (*anti*-B₁₈H₂₂) and its derivatives [2], are one of the highly investigated low molecular species nowadays, even though octadecaborane was synthesized already in the 1960s by Hawthorne and his co-workers [3]. *Anti*-B₁₈H₂₂ absorption and the emission maximum is located at 330 nm and 430 nm, respectively, and it also provides fluorescence that could be used in LED applications. However, some of its properties are not viable and several derivatives were investigated to improve solubility and to tune fluorescence, e.g. iodine- [4], pyridine- [5], sulfur- [6] derivative.

Properties of substrate-supported thin polymer films (the glass transition temperature, T_g) are influenced by chain confinement near the substrate surface, interactions between substrate and film (such as hydrogen bonding) [7], or surface roughness [8]. The T_g of a thin film can thus be lower or reach to higher values than the T_g of the bulk polymer. However, it cannot be investigated by routine measurement (DSC). Glass transition is related with the unlocking of polymer segments motion, which can cause conformational changes of chains

observable by spectroscopic methods [9,10]. Infrared Reflection-Absorption Spectroscopy (IRRAS) has been used for the investigation of thin films on reflective substrates. Besides routine measurements related with confirmation of film structure or composition [11], it can be used for monitoring of the phase separation of thin films made from polymer blends, e.g. PMMA/poly(4-vinyl phenol) [12], or other important structure- and thickness-dependent properties, such as T_g [13,14] of thin films. For instance, the strong dependence of the T_g of poly(ethylene terephthalate) was observed below 100 nm thin layers, and T_g reduction up to 25 °C in comparison with bulk was found for film thickness below 65 nm [15].

In the contribution, we focus on the behaviour of *anti*-B₁₈H₂₂ incorporated in the PS thin film. Our preliminary study deals mainly with the effect of temperature on the IR spectra of PS films and PS+B₁₈H₂₂ films on the gold substrate. The experiments were performed with the advanced technique IRRAS that provide high spectral quality. We investigated vibrational motions of PS and PS+B₁₈H₂₂ films and the effect of temperature on the change in IR spectra and the glass transition process. The purpose of all our studies in this field is to unlock the potential of borane clusters in electronics as they represent a new class of materials based neither on π - nor on σ - electron delocalization.

2. MATERIALS AND METHODS

Thin films were prepared from PS (M_w 350000, M_n 170000) purchased from Sigma-Aldrich and *anti*-B₁₈H₂₂ obtained from the Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic by spin-coating from solution. Chloroform (HPLC) from J. T. Baker was used as a solvent. The concentration of the PS solution was 30 mg/mL, and the concentration of B₁₈H₂₂ solution was 0.4 mg/mL. Solutions were mixed and stirred until full dissolution to achieve the ratio of PS:B₁₈H₂₂ equal 75:1 in the final thin film.

Thin films were deposited on gold substrates with spin coater Laurell WS-650Mz-23NPPd. The spin rate was set to 1000 rpm and the substrate was spun for 30 s. After, substrates with deposited solutions were removed and placed to vacuum oven at 40 °C to enable solvent evaporation.

The thickness of the prepared PS and PS+B₁₈H₂₂ films was measured with profilometer Dektak XT-E (Bruker).

IRRAS spectra were collected with spectrometer Nicolet iN10/iZ10 (Thermo Scientific) with a heated chamber Refractor-Reactor (Harrick) that enables reflection-absorption measurement of thin layers. The chamber is equipped with ZnSe windows and provides the angle of incidence of 75°. The spectra were recorded with a polarizer set to maximize p-polarized radiation. Thin films were heated from room temperature to 140 °C with a rate of 2.6 °C/min and spectra were recorded with resolution 4 cm⁻¹ and 16 scans. This setting enabled measurement of one spectrum per 1 °C of film heating, which eliminated adverse effects connected with spectrum measurement and simultaneous sample heating.

TGA and DSC analysis of PS pellet and *anti*-B₁₈H₂₂ powder was performed with Labsys Evo DTA/DSC instrument from Setaram. Measurement was set in the air with heating from 30 °C to 500 °C with a rate of 10 °C/min.

3. RESULTS AND DISCUSSION

Thin films of PS and PS+B₁₈H₂₂ were prepared in two series for (i) analyses of film thickness and (ii) IRRAS measurement. Thickness determination, as well as a surface visual check of thin films, was done with a mechanical profilometer and its digital camera with 100x zoom. Three repeated measurements were performed on different positions of the film surface. It was found that PS+B₁₈H₂₂ has a lower thickness of 290 nm if compared with the 450 nm PS thin film. This is probably caused by the presence of B₁₈H₂₂, which may act as a surfactant and change the properties of the spin-coated liquid layer. The surface of both films was smooth without significant differences between PS and PS+B₁₈H₂₂ samples. Both films surface evinced radial inhomogeneities which origin from the spin-coating process.

Further, IRRAS analysis was performed with both thin films. IR spectra were collected during film heating and after that spectral regions $3120 - 2985 \text{ cm}^{-1}$, $2975 - 2800 \text{ cm}^{-1}$ and $2660 - 2500 \text{ cm}^{-1}$ of $\text{C}_{\text{ar}}\text{-H}$ stretching vibrations of phenyl rings, C-H stretching vibrations of aliphatic PS part and B-H stretching vibrations of *anti*- $\text{B}_{18}\text{H}_{22}$, respectively, were examined. Spectra were baseline corrected, and area (A_{range}) was calculated. **Figure 1** depicts the dependence of $A_{3120-2985}$ and $A_{2975-2800}$ on temperature. As can be seen from the graph on the left side of **Figure 1**, the area of $\text{C}_{\text{ar}}\text{-H}$ stretching decreases with increasing temperature until the minimum is reached, then the trend is reversed and $A_{3120-2985}$ begins to grow. The temperature, which can be extracted at the minimum of this dependence, is assigned to the T_g of the thin film. The drop of region area can be explained by the fact that the density of thin films can decrease at a higher temperature and thus IR intensity of the region declines. On the other hand, the intensity of IR vibration increases as the free volume increases and segmental motion is enabled. The latter effect becomes to prevail at a temperature close to the T_g , which corresponds with the area minimum in the given plot. The T_g of PS thin film was therefore extracted to be $74 \text{ }^\circ\text{C}$, while the T_g of PS+ $\text{B}_{18}\text{H}_{22}$ was determined to be $77 \text{ }^\circ\text{C}$. *Anti*- $\text{B}_{18}\text{H}_{22}$ does not influence the PS glass transition at a significant extent. However, both of these values are $31 - 34 \text{ }^\circ\text{C}$ lower than the T_g of bulk PS $108 \text{ }^\circ\text{C}$ that was determined with a standard DSC method. This result indicates that no strong interaction between the gold substrate surface and PS are present and that high M_w of PS does not increase the thin layer T_g above the bulk T_g [16,17].

The right part of **Figure 1** is dedicated to the temperature dependence of the aliphatic C-H stretching area. The clear difference between aromatic and aliphatic C-H stretching vibrations behaviour was found. The $A_{2975-2800}$ does not evince any abrupt changes with increasing temperature, and it decreases linearly in the whole temperature range. This spectral region is thus not affected by the glass transition of PS, and no transition temperature can be determined. The reason for this different course of the plot probably originates in the structure of PS. $\text{C}_{\text{ar}}\text{-H}$ vibrations are definitely influenced with mutual positions of phenyl rings and related non-bonding interactions, while aliphatic CH_2 on PS backbone are not. Moreover, CH_2 cannot rotate. Glass transition process influences $\text{C}_{\text{ar}}\text{-H}$ vibrations to a great extent, which gives the opportunity of the T_g detection.

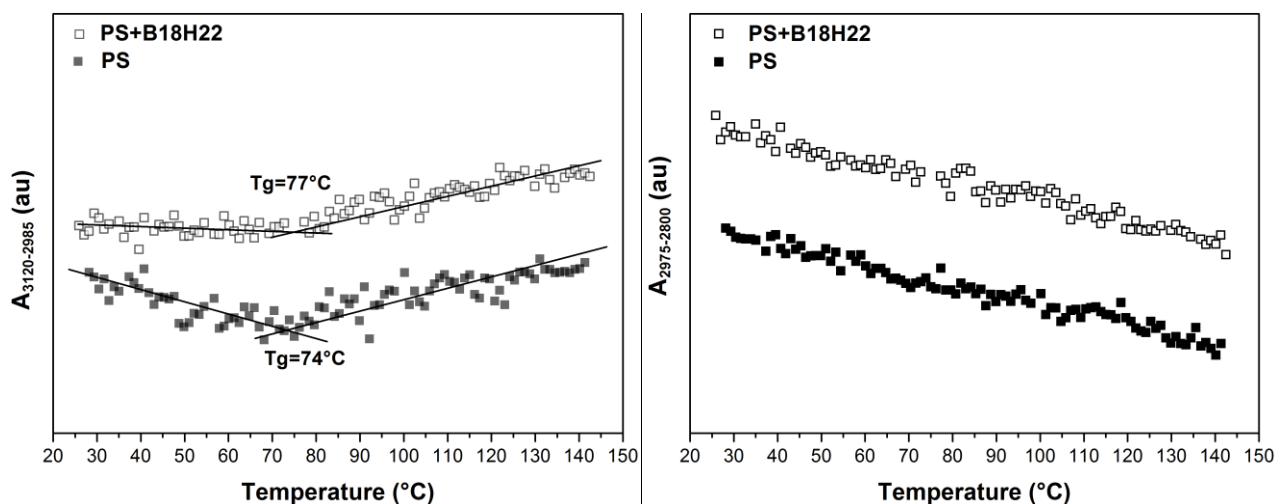


Figure 1 Area of $\text{C}_{\text{ar}}\text{-H}$ (left) and C-H (right) stretching region plotted against temperature for PS and PS+ $\text{B}_{18}\text{H}_{22}$ films

A surprising result was obtained from the detailed analysis of B-H stretching region that belongs to *anti*- $\text{B}_{18}\text{H}_{22}$ incorporated in PS+ $\text{B}_{18}\text{H}_{22}$ thin film. It has been observed during the measurement that the intensity of the absorption band at 2585 cm^{-1} decreases at higher temperatures until it is undetectable. The area of this region vs. temperature is given in **Figure 2**. The region of temperature, in which the area decrease occurs is $77 - 91 \text{ }^\circ\text{C}$. It is probably related to the T_g of PS thin film. As was stated above, the T_g was determined to $77 \text{ }^\circ\text{C}$. Above this temperature, the *anti*- $\text{B}_{18}\text{H}_{22}$ molecules are not trapped in PS matrix anymore due to the

release of segmental motions, and they start to migrate. This process might be joined with the sublimation of *anti*-B₁₈H₂₂ above 77 °C until it is fully released from the thin film.

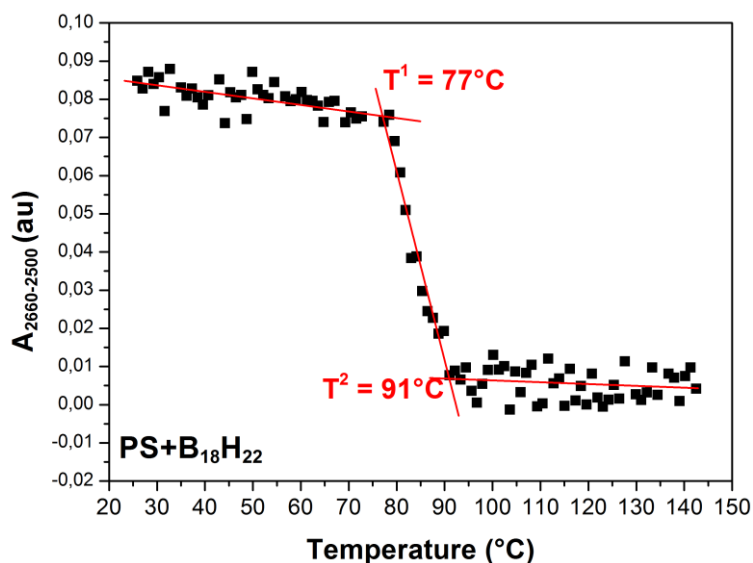


Figure 2 Area of B-H stretching region plotted against temperature for film PS+B₁₈H₂₂

To reveal the reason of the described release of *anti*-B₁₈H₂₂ from the thin film, TGA and DSC analysis of pure *anti*-B₁₈H₂₂ powder was performed in the air atmosphere to simulate similar conditions as in the case of IRRAS analysis. The curves are shown in **Figure 3**. A small weight loss of 2 % was detected at 75 °C on TGA curve and also heat flow decrease at 105 °C. This decrease in the TGA curve can be connected with sample moisture and its evaporation. It is a general fact that boranes are very sensitive to humidity, and thus thin films measured in the air atmosphere can suffer the same problem. However, there is observable a gradual decrease of the sample mass starting at about 120 °C while the main peak of *anti*-B₁₈H₂₂ melting is found at 180 °C in the DSC curve. It indicates the sublimation of the material. The mass loss step in the TGA curve smoothly continues with no disrupt change correlated with the *anti*-B₁₈H₂₂ melting, so the sublimation verges into evaporation and possible thermal degradation unnoticeably. Nevertheless, the effect of *anti*-B₁₈H₂₂ release from thin PS film needs to be explained yet, and the work on this issue continues.

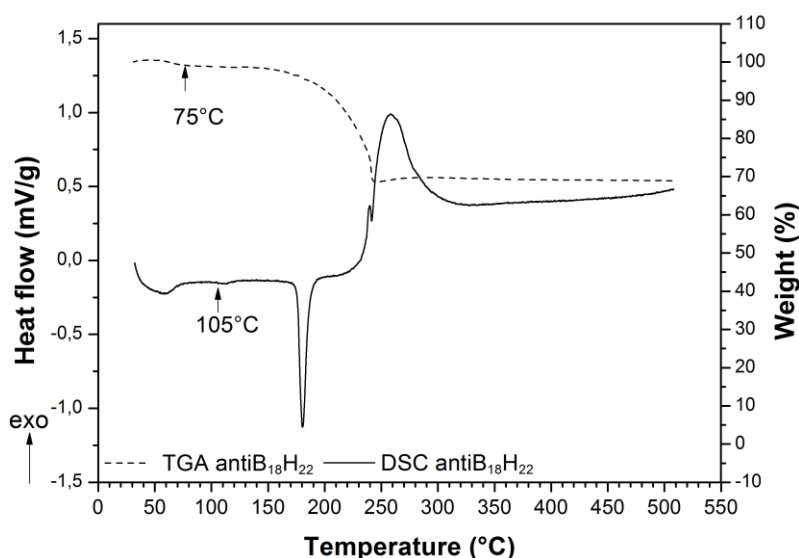


Figure 3 TGA and DSC curve of *anti*-B₁₈H₂₂ powder measured in the air

4. CONCLUSION

Thin films of PS and PS+B₁₈H₂₂ deposited on gold substrates were investigated with IRRAS analysis. IR spectra were used for the description of temperature influence on particular vibrational motions. We have focused on C_{ar}-H, C-H and B-H characteristic spectral regions and development of their area in dependence on temperature. It was found that vibrational motions respond to temperature increase differently. Whereas a clear turning point in the plot of area vs. temperature was detected for C_{ar}-H, only a slight continuous decrease of the C-H area was observed. This is probably caused by the effect of non-bonding interactions between phenyl rings that also influence vibrational motions and are more sensitive to temperature change. As a result, the determination of the T_g of PS thin film is enabled. An influence of *anti*-B₁₈H₂₂ presence on T_g of PS thin film was only marginal because the T_g of PS film was found to be 74 °C and T_g of PS+B₁₈H₂₂ 77 °C, which is 31 – 34 °C lower than T_g of bulk PS. As a result, different thin film T_g should always be considered if temperature demanding applications of polymer thin films are required.

During experiments, we also found that the intensity of the *anti*-B₁₈H₂₂ characteristic vibration decreases with increasing temperature (77 – 91 °C). *Anti*-B₁₈H₂₂ is not fixed firmly in the thin film structure and at higher temperatures, is not stable in the case of PS+B₁₈H₂₂ films. TGA and DSC analysis of pure *anti*-B₁₈H₂₂ powder revealed partial weight loss at 75 °C and heat flow decrease at 105 °C. This can be connected with the evaporation of humidity trapped in powder and a similar effect could act on the thin film. Another finding is that the T_g of PS+B₁₈H₂₂ thin film is identical with temperature, at which the B-H intensity decrease starts. It is possible that the glass transition triggers the migration and evolution of *anti*-B₁₈H₂₂ molecules from the film. However, the mechanism of *anti*-B₁₈H₂₂ release from thin PS film needs further investigation.

ACKNOWLEDGEMENTS

This work was supported by the grant from the Czech Science Foundation (Project No. 19-23513S).

The work was also supported by the Operational Program Research and Development for Innovations cofounded by the European Regional Development Fund (ERDF) and the national budget of the Czech Republic, within the framework of the project CPS - strengthening research capacity (reg. number: CZ.1.05/2.1.00/19.0409).

Michael Londesborough and Jonathan Bould from the Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic are greatly acknowledged for synthesis and providing of anti-B18H22.

REFERENCES

- [1] SKODA, D., URBANEK, P., SEVCIK, J. et al. Colloidal cobalt-doped ZnO nanoparticles by microwave-assisted synthesis and their utilization in thin composite layers with MEH-PPV as an electroluminescent material for polymer light emitting diodes. *Organic Electronics*. 2018, vol. 59, pp. 337-348.
- [2] LONDESBOROUGH, M.G.S., HNYK, D., BOULD, J. et al. Distinct Photophysics of the Isomers of B18H22 Explained. *Inorganic Chemistry*. 2012, vol. 51, no. 3, pp. 1471-1479.
- [3] PITOCELLI, A.R. & HAWTHORNE, M.F. Preparation of a New Boron Hydride B18h22. *Journal of the American Chemical Society*. 1962, vol. 84, no. 16, p. 3218.
- [4] LONDESBOROUGH, M.G.S., DOLANSKY, J., BOULD, J. et al. Effect of Iodination on the Photophysics of the Laser Borane anti-B18H22: Generation of Efficient Photosensitizers of Oxygen. *Inorganic Chemistry*. 2019, vol. 58, no. 15, pp. 10248-10259.
- [5] LONDESBOROUGH, M.G.S., DOLANSKY, J., JELINEK, T. et al. Substitution of the laser borane anti-B18H22 with pyridine: a structural and photophysical study of some unusually structured macropolyhedral boron hydrides. *Dalton Transactions*. 2018, vol. 47, no. 5, pp. 1709-1725.

- [6] SAURI, V., OLIVA, J.M., HNYK, D. et al. Tuning the Photophysical Properties of anti-B18H22: Efficient Intersystem Crossing between Excited Singlet and Triplet States in New 4,4'-(HS)(2)-anti-B18H20. *Inorganic Chemistry*. 2013, vol. 52, no. 16, pp. 9266-9274.
- [7] KEDDIE, J.L., JONES, R., & CORY, R.A. Interface and Surface Effects on the Glass-Transition Temperature in Thin Polymer-Films. *Faraday Discussions*. 1994, vol. 98, pp. 219-230.
- [8] HANAKATA, P.Z., DOUGLAS, J.F., & STARR, F.W. Interfacial mobility scale determines the scale of collective motion and relaxation rate in polymer films. *Nature Communications*. 2014, vol. 5, pp. 4163.
- [9] OLMOS, D., MARTIN, E.V., & GONZALEZ-BENITO, J. New molecular-scale information on polystyrene dynamics in PS and PS-BaTiO₃ composites from FTIR spectroscopy. *Physical Chemistry Chemical Physics*. 2014, vol. 16, no. 44, pp. 24339-24349.
- [10] SHIN, H.S., LEE, H., JUN, C.H. et al. Transition temperatures and molecular structures of poly(methyl methacrylate) thin films by principal component analysis: comparison of isotactic and syndiotactic poly(methyl methacrylate). *Vibrational Spectroscopy*. 2005, vol. 37, no. 1, pp. 69-76.
- [11] DA SILVA, E.A., CASELI, L., & OLIVATI, C.d.A. Organization of polythiophenes at ultrathin films mixed with stearic acid investigated with polarization-modulation infrared reflection-absorption spectroscopy. *Colloids and Surfaces A-Physicochemical and Engineering Aspects*. 2017, vol. 529, pp. 628-633.
- [12] TERASAKI, M., Khasanah, OZAKI, Y. et al. Study on phase separation in an ultra-thin poly(methyl methacrylate)/poly(4-vinyl phenol) film by infrared reflection absorption spectroscopy. *Polymer*. 2018, vol. 135, pp. 69-75.
- [13] PENG, Y., LIU, Y., WU, Q. et al. Study on the Glass Transition Process of Polymer System Using Differential Scanning Calorimetry and Fourier Transform Infrared Spectroscopy. *Analytical Sciences*. 2017, vol. 33, no. 9, pp. 1071-1076.
- [14] TRETINNIKOV, O.N. & OHTA, K. Conformation-sensitive infrared bands and conformational characteristics of stereoregular poly(methyl methacrylate)s by variable-temperature FTIR spectroscopy. *Macromolecules*. 2002, vol. 35, no. 19, pp. 7343-7353.
- [15] ZHANG, Y., ZHANG, J.M., LU, Y.L. et al. Glass transition temperature determination of poly(ethylene terephthalate) thin films using reflection-absorption FTIR. *Macromolecules*. 2004, vol. 37, no. 7, pp. 2532-2537.
- [16] MATTSSON, J., FORREST, J.A., & BORJESSON, L. Quantifying glass transition behavior in ultrathin free-standing polymer films. *Physical Review E*. 2000, vol. 62, no. 4, pp. 5187-5200.
- [17] FORREST, J.A., DALNOKIVERESS, K., & DUTCHER, J.R. Interface and chain confinement effects on the glass transition temperature of thin polymer films. *Physical Review E*. 1997, vol. 56, no. 5, pp. 5705-5716.