Tri-α-Napthyl Benzene as a Glassy or Crystalline Matrix for MALDI TOF MS of Synthetic Polymers

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Introduction

The matrix compound employed in matrix assisted laser desorption/ionization (MALDI) mass spectrometry disperses and supports the polymer molecules and, therefore, sample preparation is crucial to the success of the technique. The sample preparation involves a complicated system of polymer-matrix-solvent that undergoes simultaneous evaporation-crystallization-phase separation that can produce a wide variety of morphologies. Recent work at NIST has used small angle neutron scattering (SANS) to measure the dispersion of polymers in a crystalline matrix. A common MALDI combination, polystyrene in a dithranol matrix, was found to produce large domains of polymer, containing hundreds or thousands of aggregated chains. Since MALDI matrices are virtually always crystalline, the dispersion size of the polymers in virtually all MALDI measurements may be quite large. This may not be the optimum morphology for a MALDI measurement, but examples of molecularly dispersed chains in a MALDI matrix are rare.

Previous work on MALDI of synthetic polymers [1] has examined liquid matrices by using mixtures of relatively non-volatile liquids and UV adsorbers. They found that a higher UV power was required for these matrices than for conventional crystalline matrices and that crystalline matrices had better resolution and could analyze higher molecular weight polymers. But there is no direct proof that there is an absence of crystallinity and/or phase separation in the samples prepared with liquid matrices.

In this paper we introduce a new MALDI matrix, tri-α-napthyl benzene (TαNB) that can form a glassy MALDI matrix at ambient temperatures. In addition, it can be made to crystallize making it a unique material that can be either crystalline or amorphous producing morphologies that are either highly aggregated chains that are strongly phase separated or individual chains dissolved in the matrix.

Methods

Tri-α-napthyl benzene was synthesized by a method derived by Elmorsy et al [2]. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC 7 calorimeter [3] from (30 to 200) °C at 10 °C/min under nitrogen. SANS experiments were carried out on the 8m (NG1) instrument of the National Institute of Standards and Technology Cold Neutron Research Facility in Gaithersburg, MD. Poly(styrene-d_8) (PSD) at a mass fraction 1 % PSD in TαNB was electrosprayed onto a copper disk for the SANS experiment and onto a conventional MALDI target for molecular mass determination. MALDI was performed on a Bruker Reflex II MALDI-TOF Mass Spectrometer operated in linear mode, with a dual microchannel plate detector and a 3 ns pulse width nitrogen laser. All mass spectra were acquired using delayed extraction.

Results

Figure 1 shows DSC analysis of TαNB that was electrosprayed from methylene chloride and transfered from the substrate into a DSC pan. The scan showed crystalline melting on the first run with a complete disappearance of crystalline melting upon the second scan. Therefore, the crystalline state of the sample can be easily controlled by sample preparation and treatment, with a highly crystalline sample being initially created that can be converted to a glassy sample by annealing above the melting point for a few minutes. The DSC pan was pried open and a drop of 1-butanol was placed on the glassy TαNB. After evaporation, the transparent sample became white and the crystalline melting reappeared. Figure 2 shows the SANS of the electrosprayed and the melted PSD/TαNB samples. The error bars are one

standard deviation. The high q slopes of the two morphologies are –4 for the electrosprayed and –2 for the melted samples signifying strongly phase separated and dissolved PSD respectively [4]. Therefore, electrosprayed samples are strongly phase separated into large domains while the samples that were annealed above the crystalline melting point formed solid solutions. Therefore, TαNB is an ideal model matrix for the study of the effect of polymer dispersion on the efficiency of MALDI.

Figure 3 shows the MALDI results from electrosprayed, melted, and recrystallized samples. The electrosprayed sample gives a strong MALDI signal typical of similar polystyrene samples in conventional matrices such as dithranol. Upon annealing, the film became optically transparent, suggesting that a miscible mixture had been formed. The middle plot shows the signal of the annealed sample for the same number of laser pulses. The near complete loss of signal could possibly be due to irreparable changes in the sample due to the heat treatment such as loss of the cationizing agent or the degradation of the polystyrene. The samples were modified by placing a drop of 1-butanol on the surface of the film. 1-butanol is a good solvent for the TαNB but a nonsolvent for the polystyrene. Upon evaporation of the solvent, the film had become opaque, suggesting that the two phase morphology had been regained. MALDI of this sample produced a strong signal, comparable to the original electrosprayed sample.

Therefore, the disappearance of the MALDI signal with melting of the TαNB matrix is not due to an irreversable change in the sample. Rather, it seems likely that polymer chains that are molecularly dispersed in a matrix produce far less signal than ones grouped in large domains separated by crystallites.

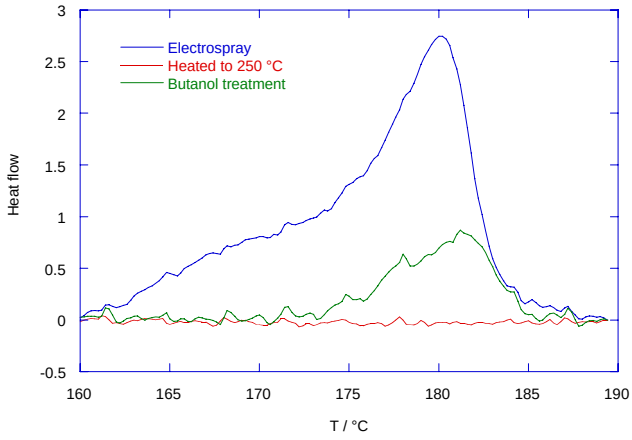

Figure 1. DSC of electrosprayed, melted, and butanol treated TαNB

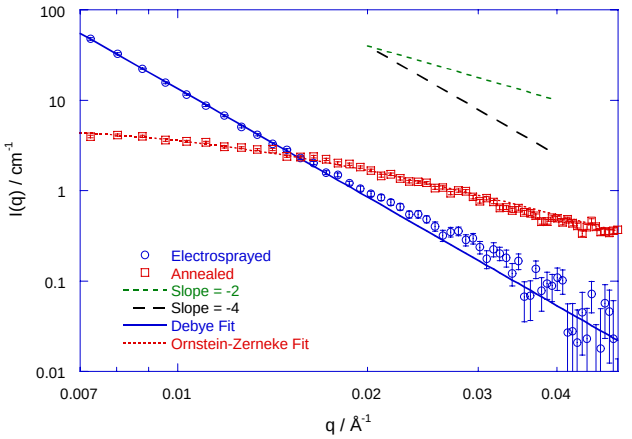

Figure 2. SANS of electrosprayed and melted 1 % PSD / TαNB

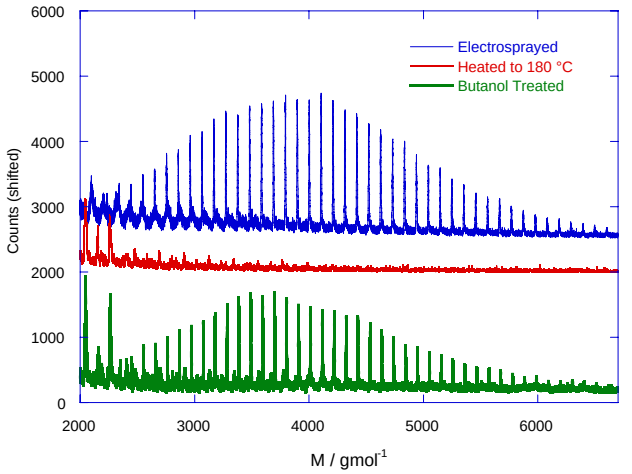

Figure 3. MALDI of electrosprayed, melted, and butanol treated 1 % PSD / TαNB

References

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2. Elmorsy S. S., Khalil A. G. M., Girges M. M., Salama T. A., *Tet. Lett*, **1997**, *38*, 1071.
3. Certain commercial items are identified in this paper in order to adequately specify the experimental procedure. This does not imply endorsement by NIST.
4. Higgins, J. S., Benoit, H. C., *Polymers and Neutron Scattering*, Clarendon Press, Oxford, 1996.