

Abstract:

There is currently a very limited set of engineering polymers that have been demonstrated as viable for use in 3-D printing. Additive manufacturing of custom components will require a much larger array of polymers, especially those with physical, thermal, chemical, and mechanical properties that can be tailor-made. The development of ‘Ionic Polyimides’ offers a solution to this shortage by combining the well understood and widely accepted properties of conventional polyimides, with a new approach to polymer synthesis. Polyimides and polymeric ionic liquids (poly(ILs)) are at the forefront of advanced polymer materials, each with their own set of advantages and disadvantages. While it is clear that more types of polymer materials are needed for fused deposition modeling (FDM) additive manufacturing, there is a need to explore these classes of materials. The synthesis process developed by the Bara Research Group at the University of Alabama allows full control over polymer structure, nanostructure, thermal, electrical, and physical properties making them a prime candidate for use in the additive manufacturing process. Furthermore, the new process allows us to tailor-make a high strength polymer that can be used to fabricate filament feedstock instead of pellets for 3D printing.

The primary objective of this proposal is to determine the relationship between molecular structure, physical properties, and performance of ionic polyimides. Further, we seek to determine their utility as materials suitable for additive manufacturing of components used in aerospace vehicles, with an emphasis on characterizing and simulating their thermal behaviors and properties. This proposal addresses the need for fundamental research on a customizable polymer filament feedstock for 3-D printing with tailor-made properties potentially making it superior to the commercial blends offered in industry today. The deliverables for this project are the creation of a database that will detail the relationships between the molecular structure and physical properties for the ionic polyimide of interest (e.g. Tg/Tm relative to different ionic polyimide structures). This new database will provide a “road map” to the development of the first generation of materials and ultimately proof-of-concept.

Ionic Polyimides: New High Performance Polymers for Additive Manufacturing

PI:

Enrique Jackson, Ph.D. EM22

Collaborators:

Jason Bara, Ph.D. – The University of Alabama – Tuscaloosa

Kendall Byler, Ph.D. – The University of Alabama – Huntsville

Aaron Adams, Ph.D. – Alabama A&M University

Erica West – Florida A&M University

Tim Huff – EM22

Brian Thomas – Alabama A&M University

Agenda

- Abstract
- Introduction
- Experimental Activities
 - Synthesis
 - Thermal Characterizations
 - DSC
 - TG-IR
 - Modeling
- Future Work

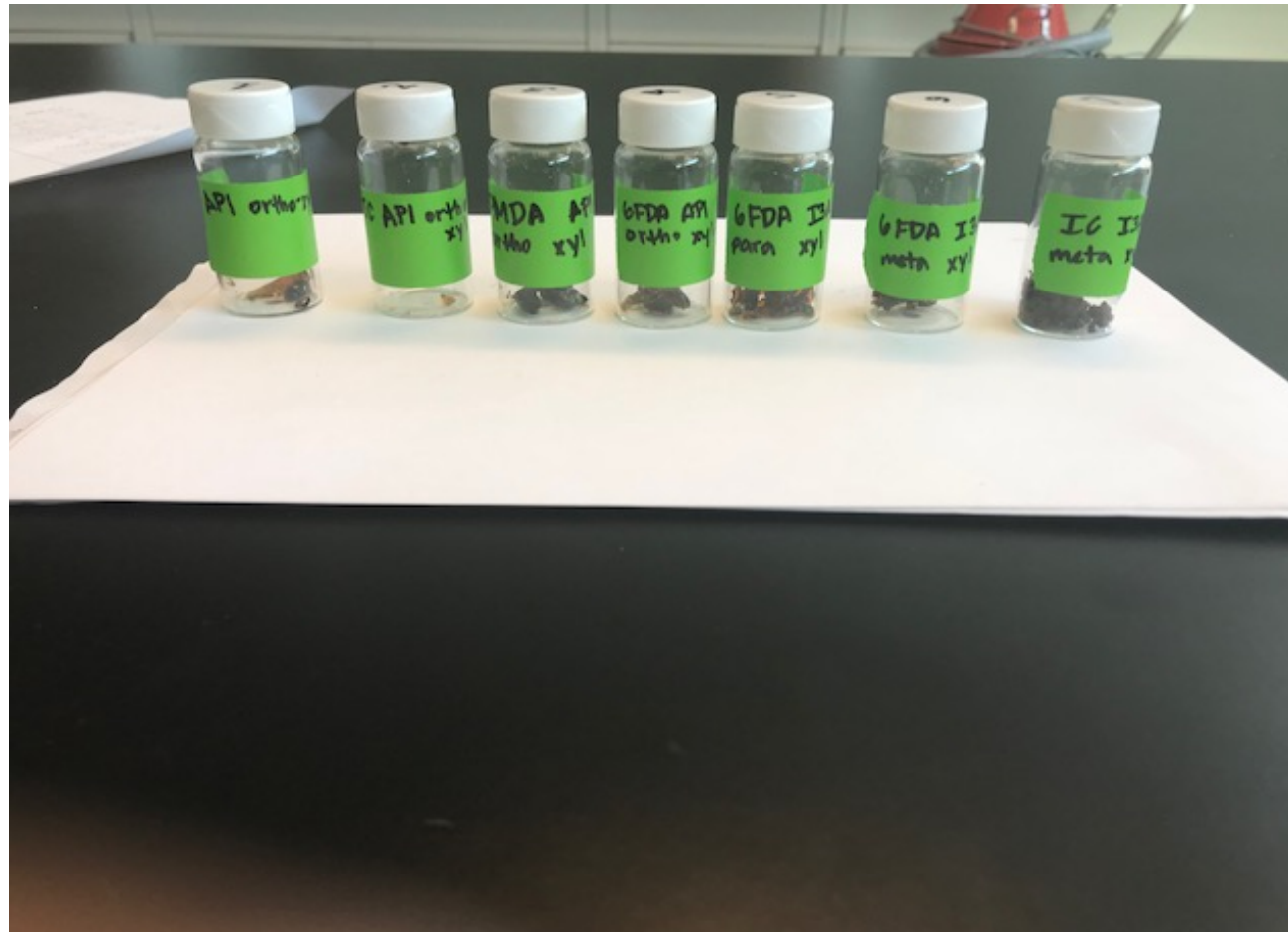
Abstract

- There is currently a very limited set of engineering polymers that have been demonstrated as viable for use in 3-D printing
- Additive manufacturing of custom components will require a much larger array of polymers, especially those with physical, thermal, chemical, and mechanical properties that can be tailor-made
- The development of 'Ionic Polyimides' offers a solution to this shortage by combining the well understood and widely accepted properties of conventional polyimides, with a new approach to polymer synthesis

Abstract cont.

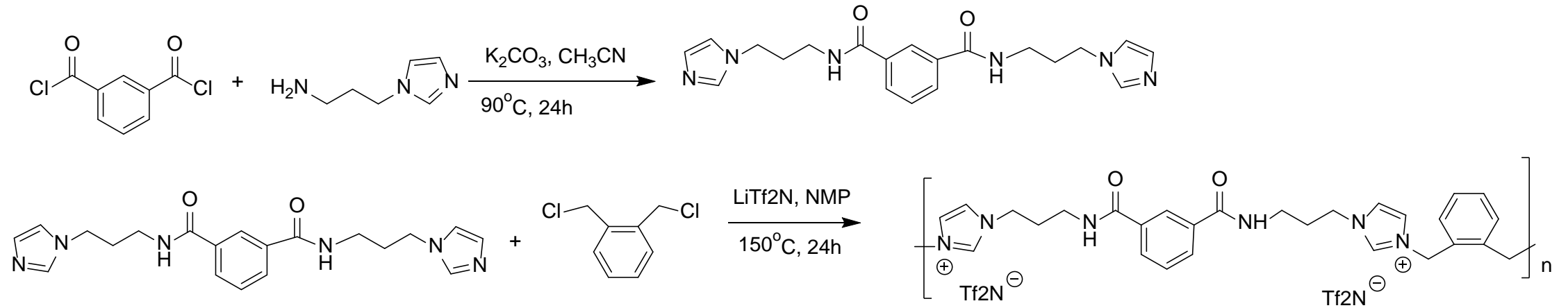
- Polyimides and polymeric ionic liquids (poly(ILs)) are at the forefront of advanced polymer materials, each with their own set of advantages and disadvantages
- While it is clear that more types of polymer materials are needed for fused deposition modeling (FDM) additive manufacturing, there is a need to explore these classes of materials
- The synthesis process developed by the Bara Research Group at the University of Alabama allows full control over polymer structure, nanostructure, thermal, electrical, and physical properties making them a prime candidate for use in the additive manufacturing process

Ionic Polyimides



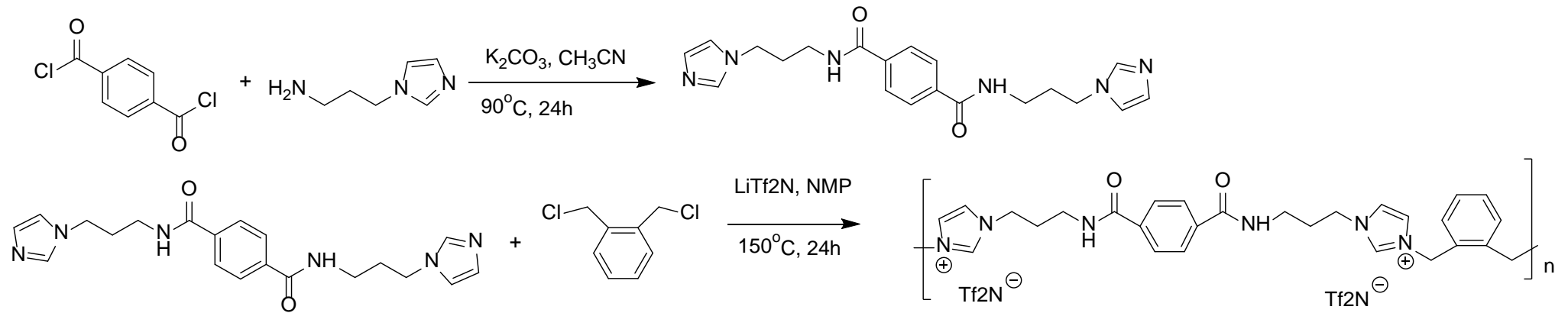
Ionic Polyimide Synthesis

IC API ortho xylene



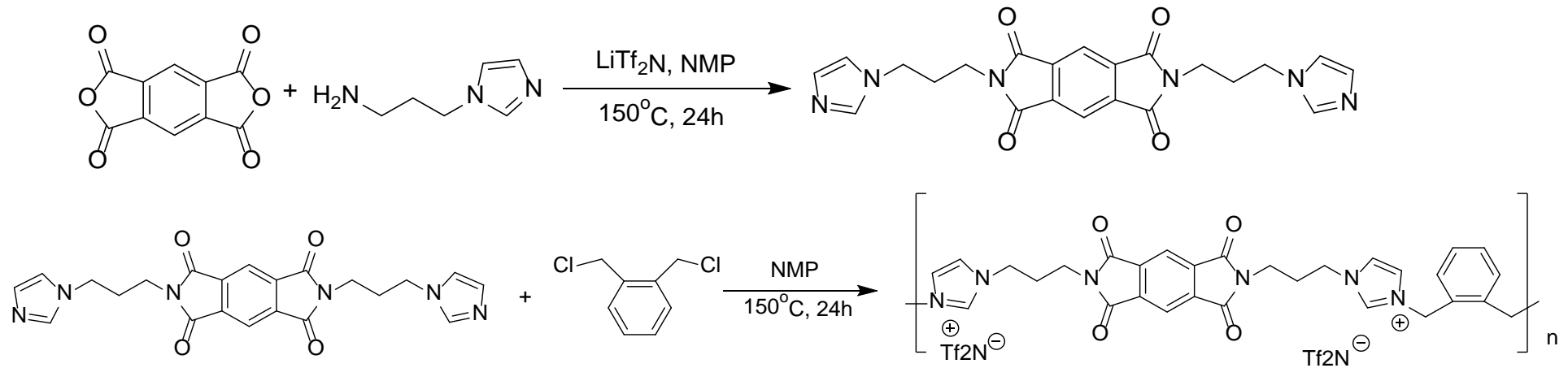
Ionic Polyimide Synthesis

TC API ortho xylene



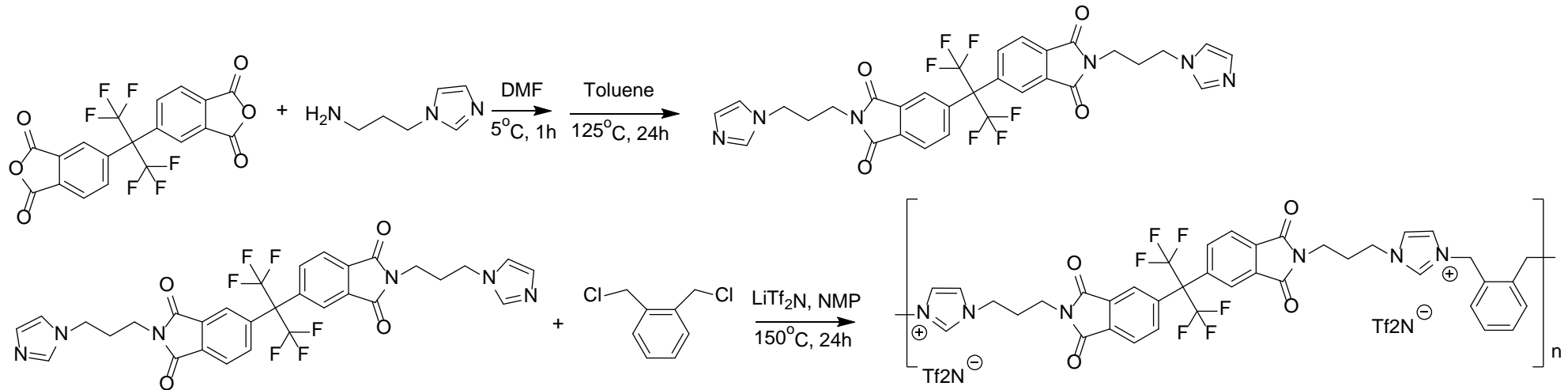
Ionic Polyimide Synthesis

PMDA API ortho xylene



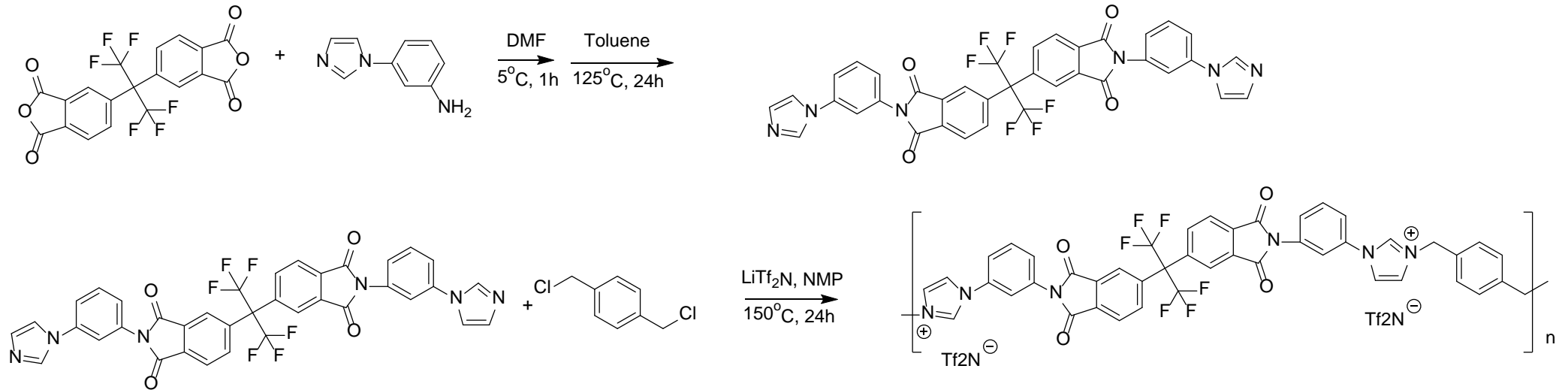
Ionic Polyimide Synthesis

6FDA API ortho xylene



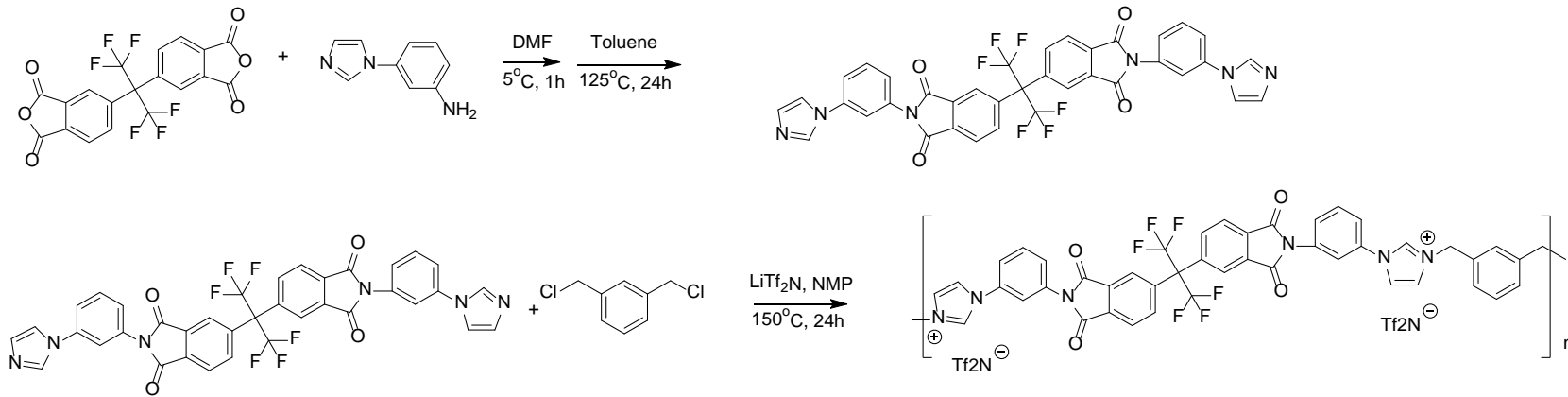
Ionic Polyimide Synthesis

6FDA I3A para xylene



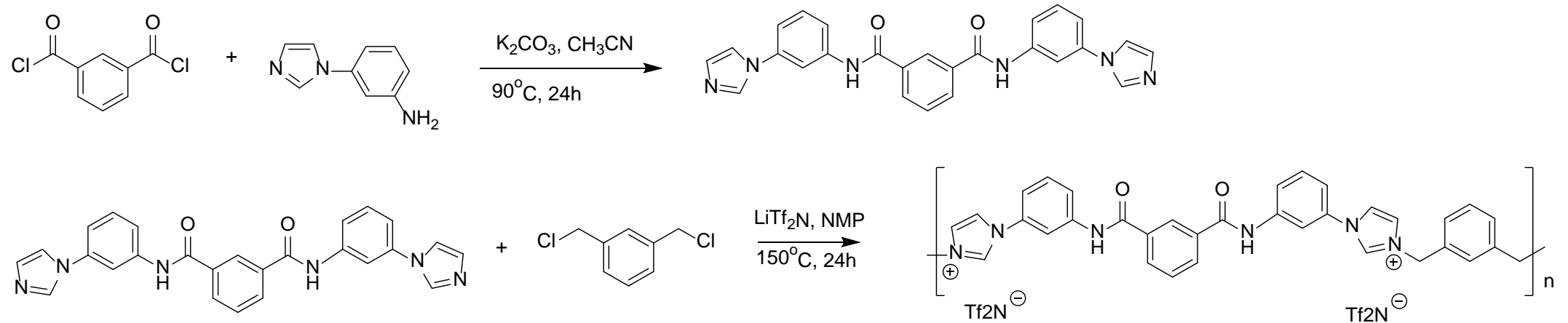
Ionic Polyimide Synthesis

6FDA I3A meta xylene



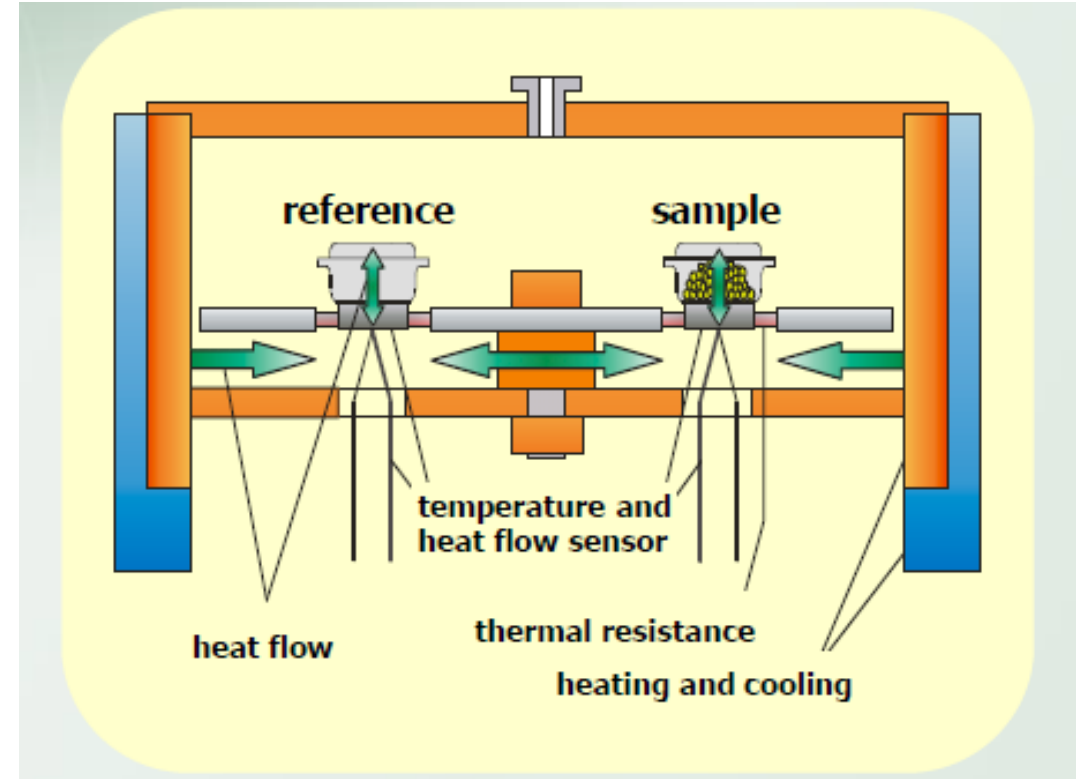
Ionic Polyimide Synthesis

IC I3A meta xylene



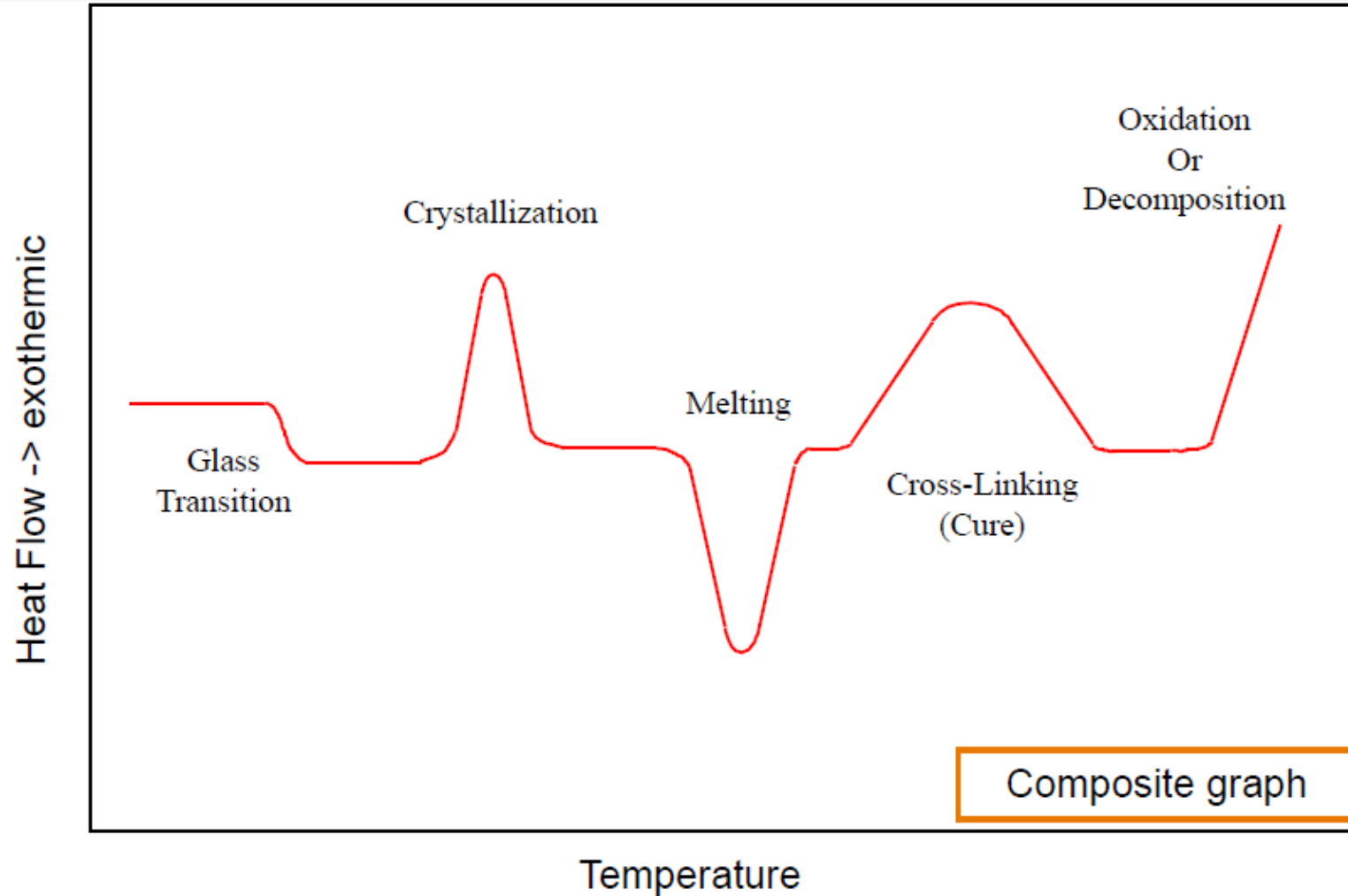
Thermal Characterization Techniques – Differential Scanning Calorimetry (DSC)

DSC is a technique in which the difference in energy inputs into a substance and a reference materials reassured as a function of temperature while the substance and reference is subjected to a controlled-temperature program



Netzsch, Inc. Thermal Analysis – An Introduction
3-7-2005

Typical DSC Transitions



DSC Training – TA Instruments

DSC Results – Starting Materials

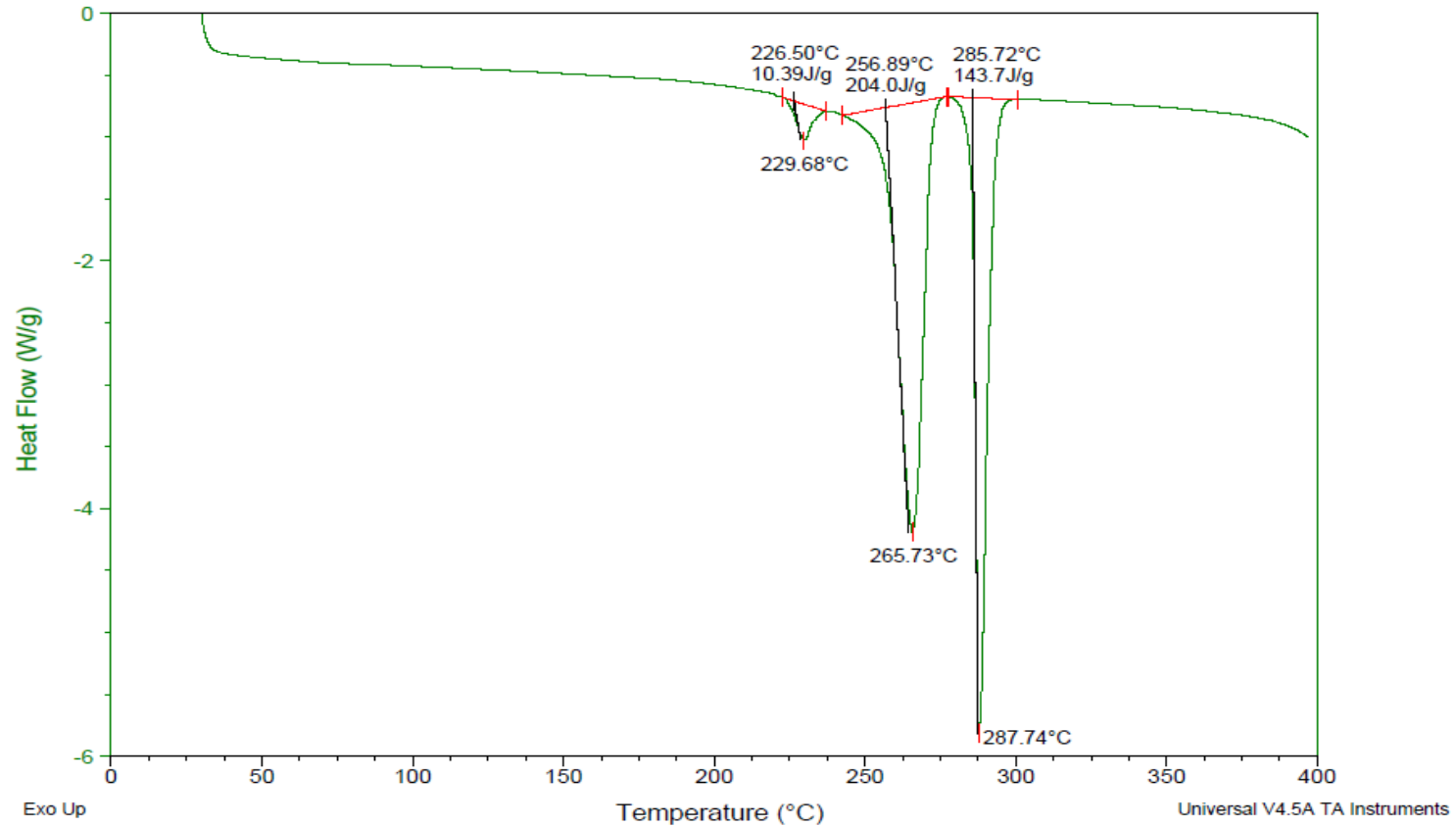
Samples	Endothermic Transition 1 (J/g)	Endothermic Transition 2 (J/g)	Endothermic Transition 3 (J/g)	Exothermic Transition (J/g)
Sample 1 Onset Temperatures (°C)	10.34 ± 0.08	196.45 ± 10.68	140.65 ± 4.31	
	229.15 ± 0.33	265.83 ± 0.13	287.85 ± 0.16	
Sample 2 Onset Temperatures (°C)	37.59 ± 4.43			48.08 ± 0.92
	229.15 ± 0.33			374.22 ± 4.07
Sample 3 Onset Temperatures (°C)	356			
	304.67			
Sample 5 Onset Temperatures (°C)	12.65 ± 1.27	61.73 ± 21.45		
	74.54 ± 1.02	171.95 ± 0.21		
Sample 6 Onset Temperatures (°C)	186.5 ± 1.13	153.2 ± 4.80		
	116.79 ± 18.83	232.97 ± 16.67		
Sample 7 Onset Temperatures (°C)	105.85 ± 1.91	218.4 ± 55.58		
	47.75 ± 0.16	282.66 ± 4.11		
Sample 8 Onset Temperatures (°C)	490.45 ± 232.28			
	256.81 ± 2.96			
Sample TC Onset Temperatures (°C)	9.79 ± 0.26	122.65 ± 3.18	280.05 ± 0.92	
	71.06 ± 0.16	85.96 ± 0.41	277.37 ± 0.56	
Sample 6FDA Onset Temperatures (°C)	110.45 ± 6.71			
	247.56 ± 0.19			

DSC Results – Starting Materials

Sample: Sample 1
Size: 11.2000 mg
Method: Polyimides
Comment: Sample 1 Test 1

DSC

File: C:\...13-20-2017\Sample 1 Test 1
Operator: Jackson
Run Date: 20-Mar-2017 11:14
Instrument: DSC Q20 V24.11 Build 124

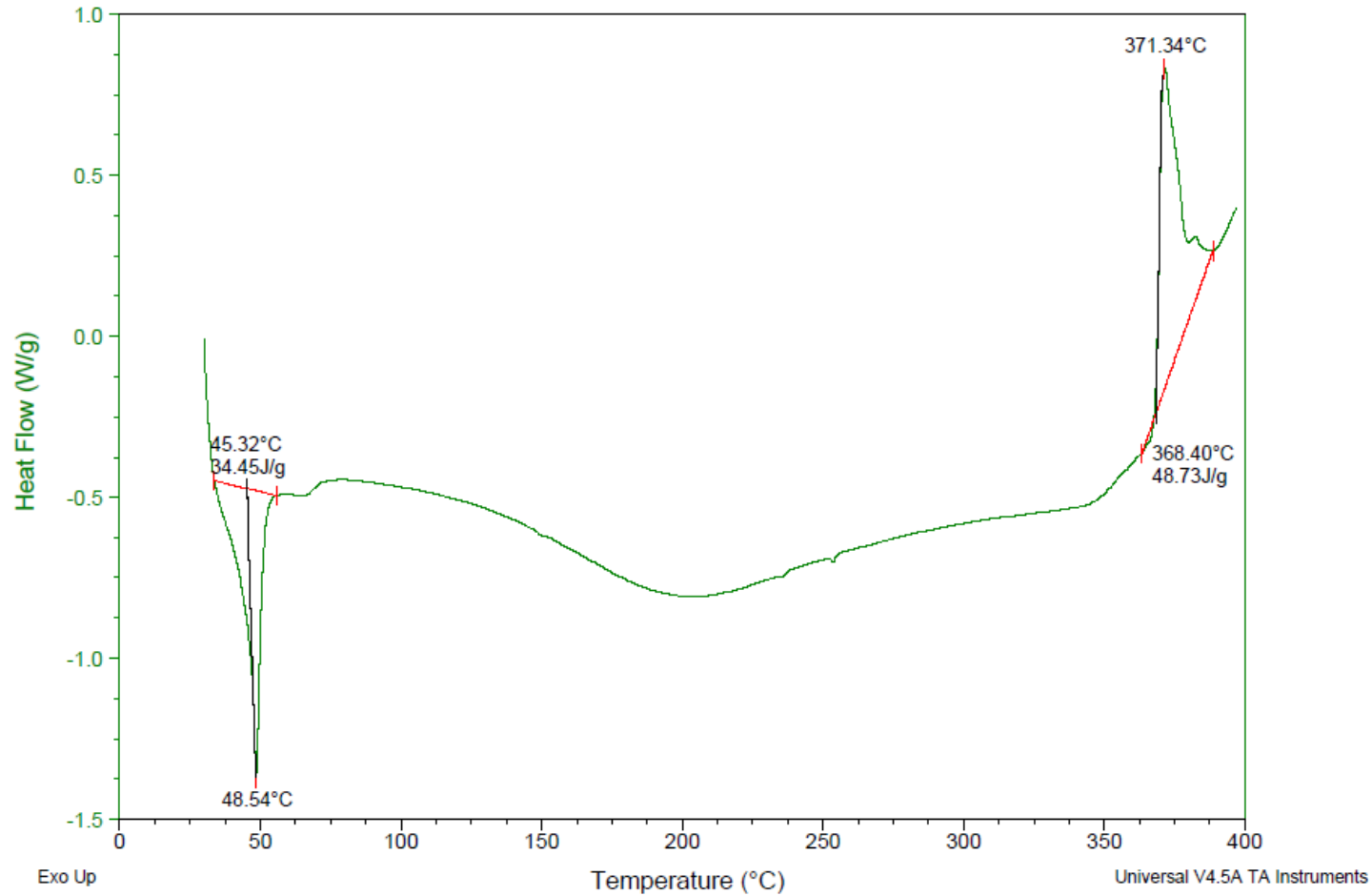


DSC Results – Starting Materials

Sample: Sample 2 Test 4
Size: 7.2000 mg
Method: Polyimides
Comment: Sample 2 Test 4

DSC

File: E:\3-20-2017\3-28-2017\Sample 2 Test 4
Operator: Jackson
Run Date: 28-Mar-2017 05:59
Instrument: DSC Q20 V24.11 Build 124

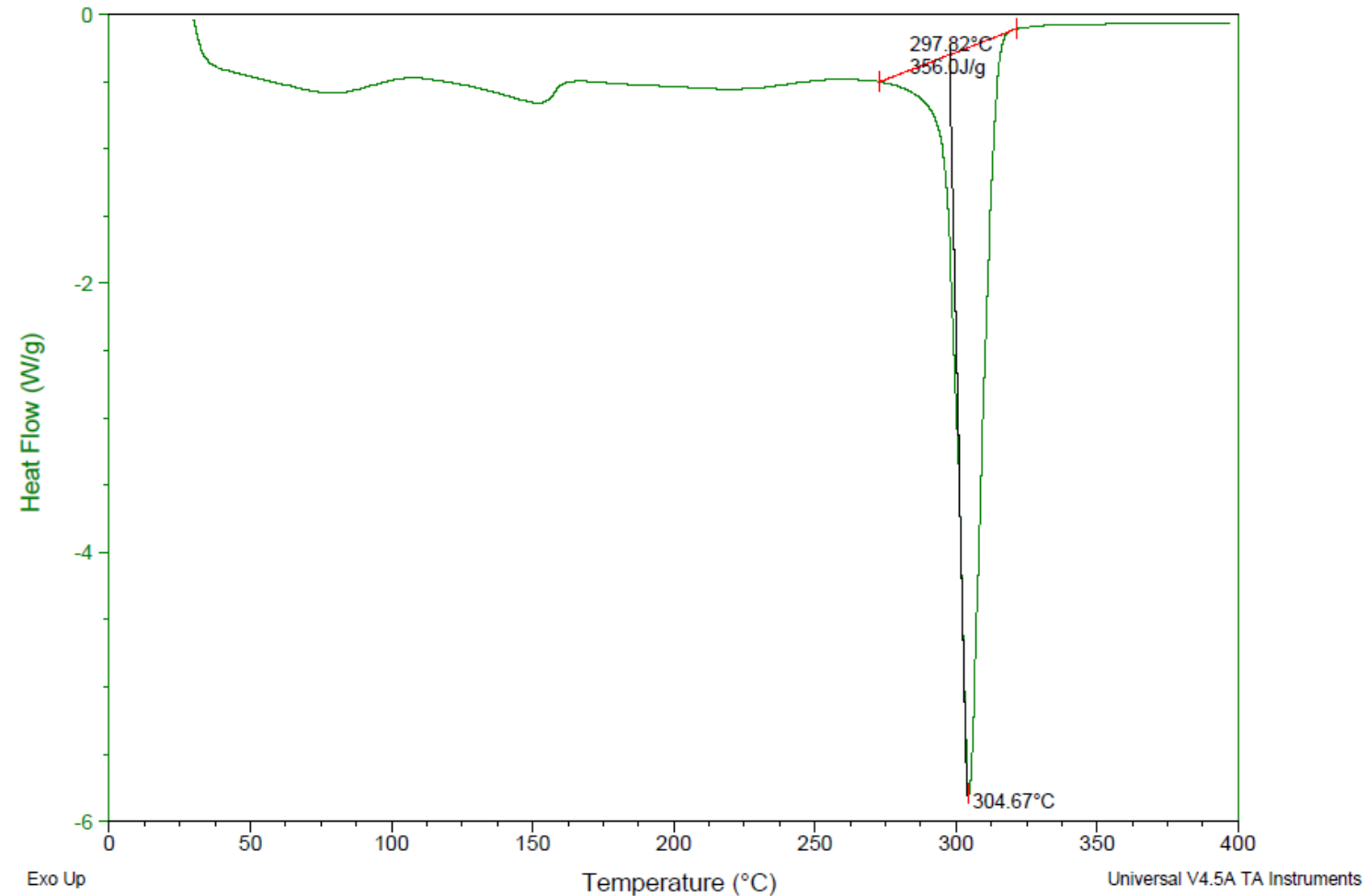


DSC Results – Starting Materials

Sample: Sample 3 Test 1
Size: 30.6000 mg
Method: Polyimides
Comment: Sample 3 Test 1

DSC

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Operator: Jackson
Run Date: 28-Mar-2017 07:32
Instrument: DSC Q20 V24.11 Build 124

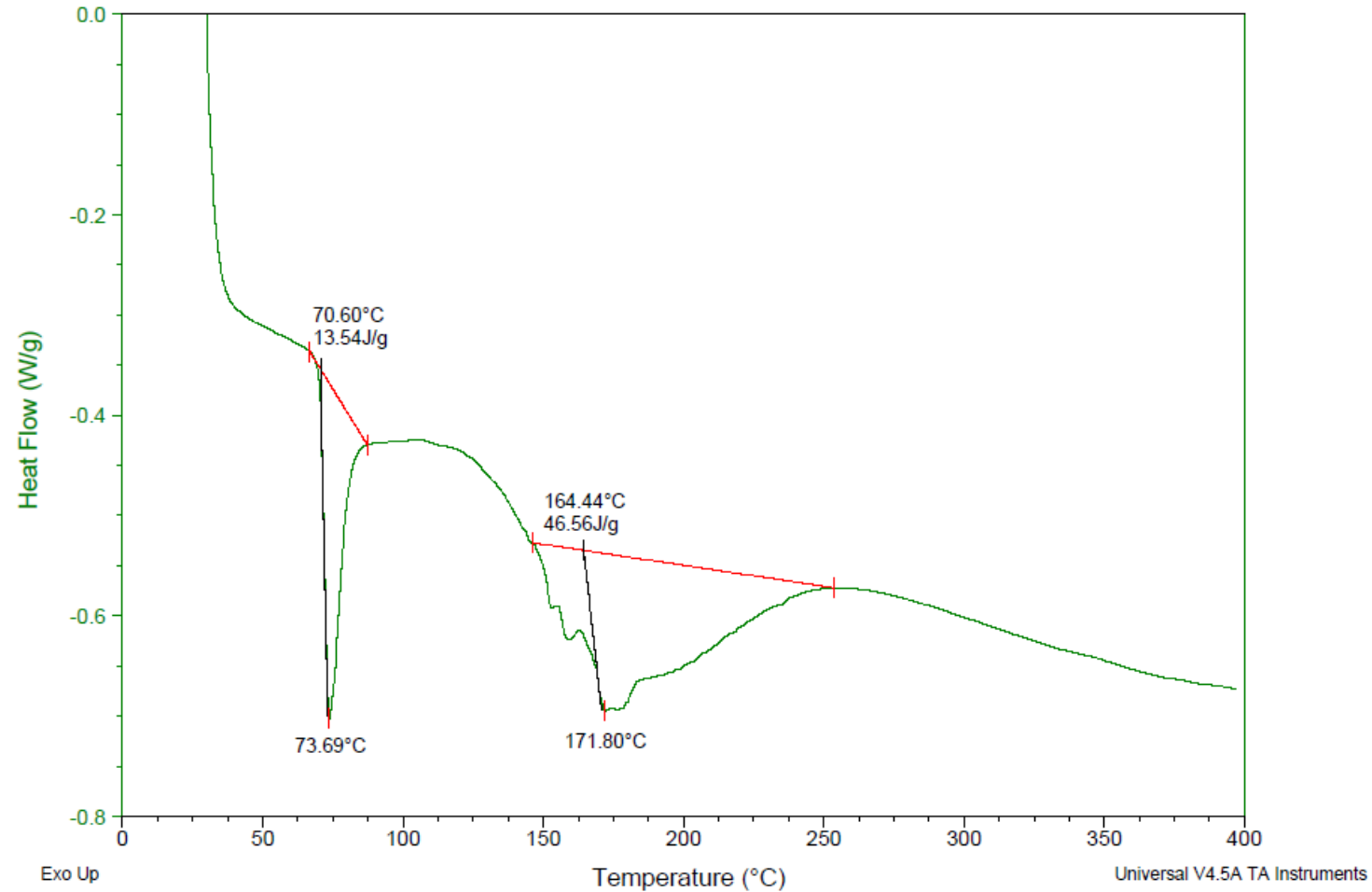


DSC Results – Starting Materials

Sample: Sample 5
Size: 17.3000 mg
Method: Polyimides
Comment: Sample 5 Test 1

DSC

File: C:\...3-20-2017\Sample 5 Test 1
Operator: Jackson
Run Date: 21-Mar-2017 07:45
Instrument: DSC Q20 V24.11 Build 124

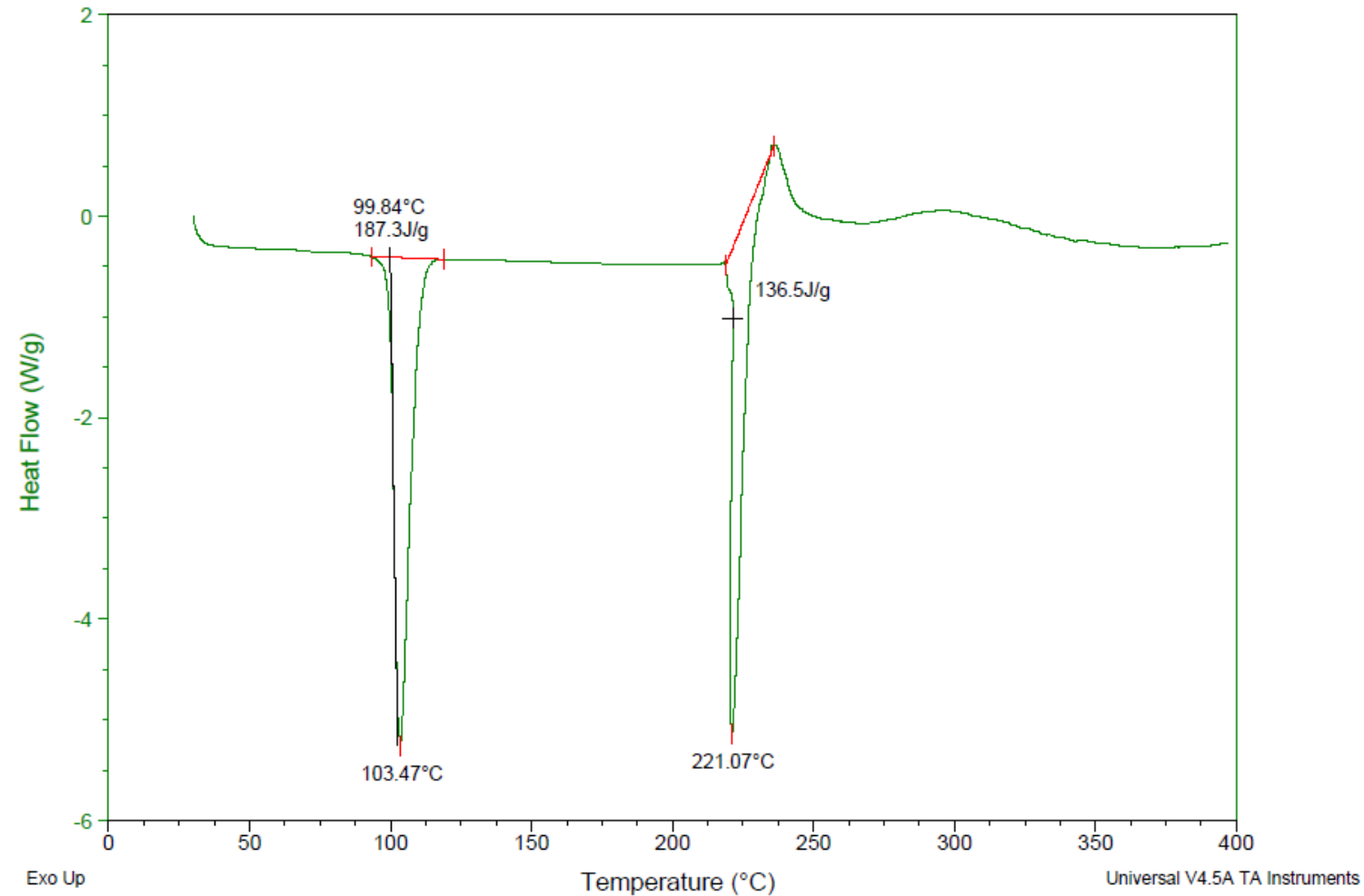


DSC Results – Starting Materials

Sample: Sample 6
Size: 14.7000 mg
Method: Polyimides
Comment: Sample 6 Test 1

DSC

File: C:\...13-20-2017\Sample 6 Test 1 data
Operator: Jackson
Run Date: 21-Mar-2017 14:59
Instrument: DSC Q20 V24.11 Build 124

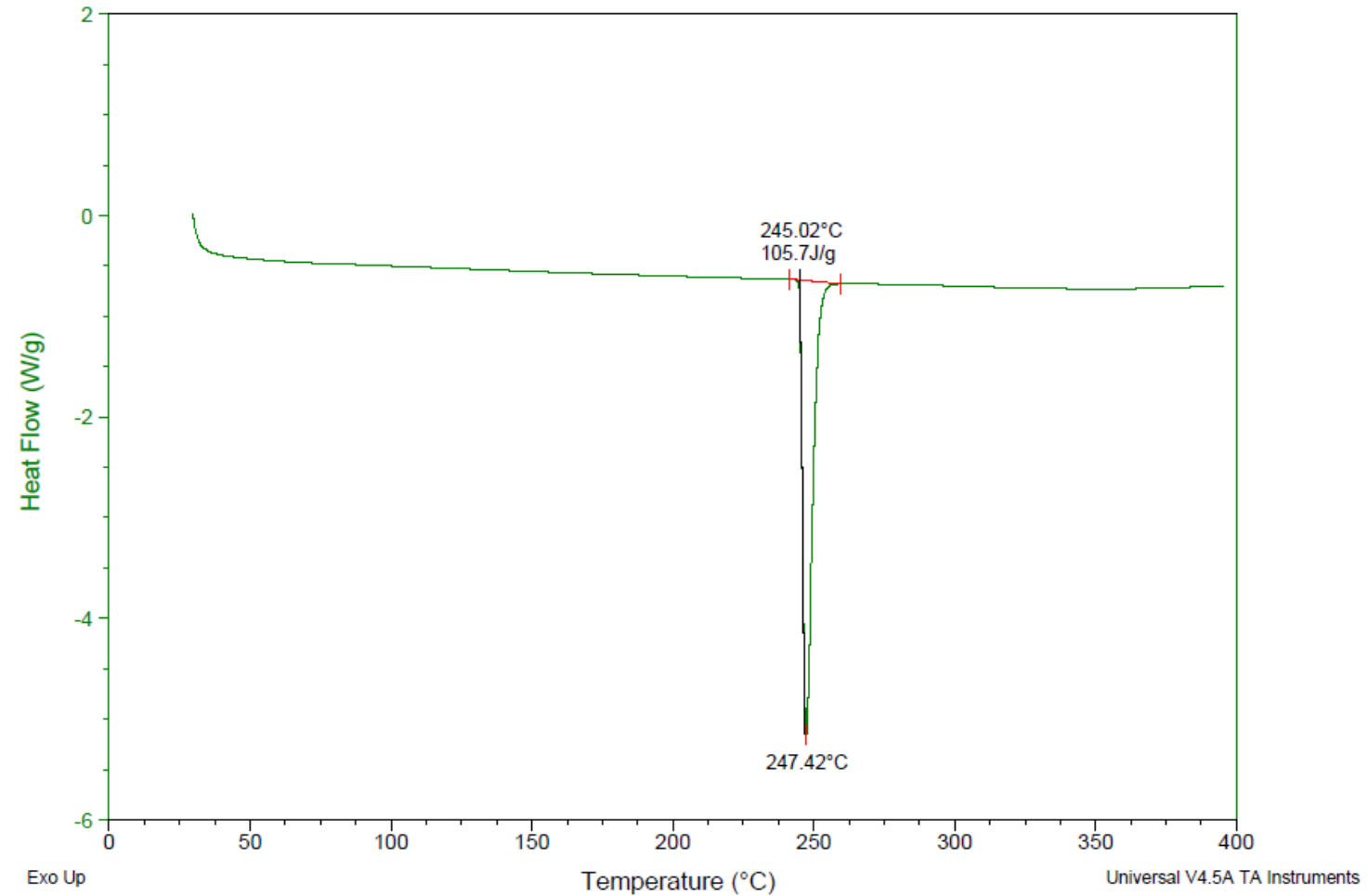


DSC Results – Starting Materials

Sample: Sample 6FDA Test 1
Size: 7.1000 mg
Method: Polyimides
Comment: Sample 6FDA Test 1

DSC

File: C:\...13-20-2017\Sample 6FDA Test 1
Operator: Jackson
Run Date: 23-Mar-2017 14:42
Instrument: DSC Q20 V24.11 Build 124

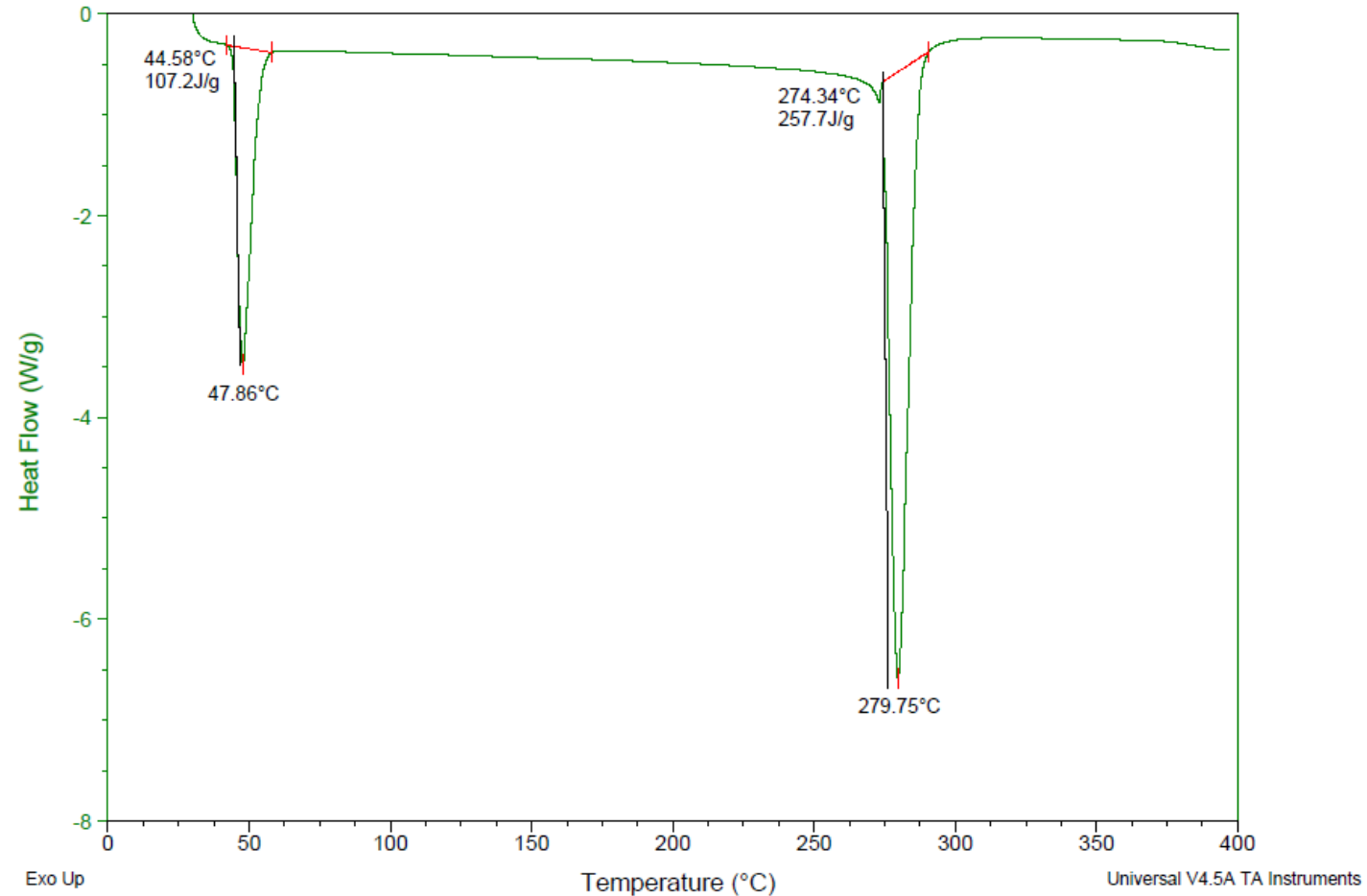


DSC Results – Starting Materials

Sample: Sample 7
Size: 14.0000 mg
Method: Polyimides
Comment: Sample 7 Test 1

DSC

File: C:\...13-20-2017\Sample 7 Test 1
Operator: Jackson
Run Date: 22-Mar-2017 07:45
Instrument: DSC Q20 V24.11 Build 124

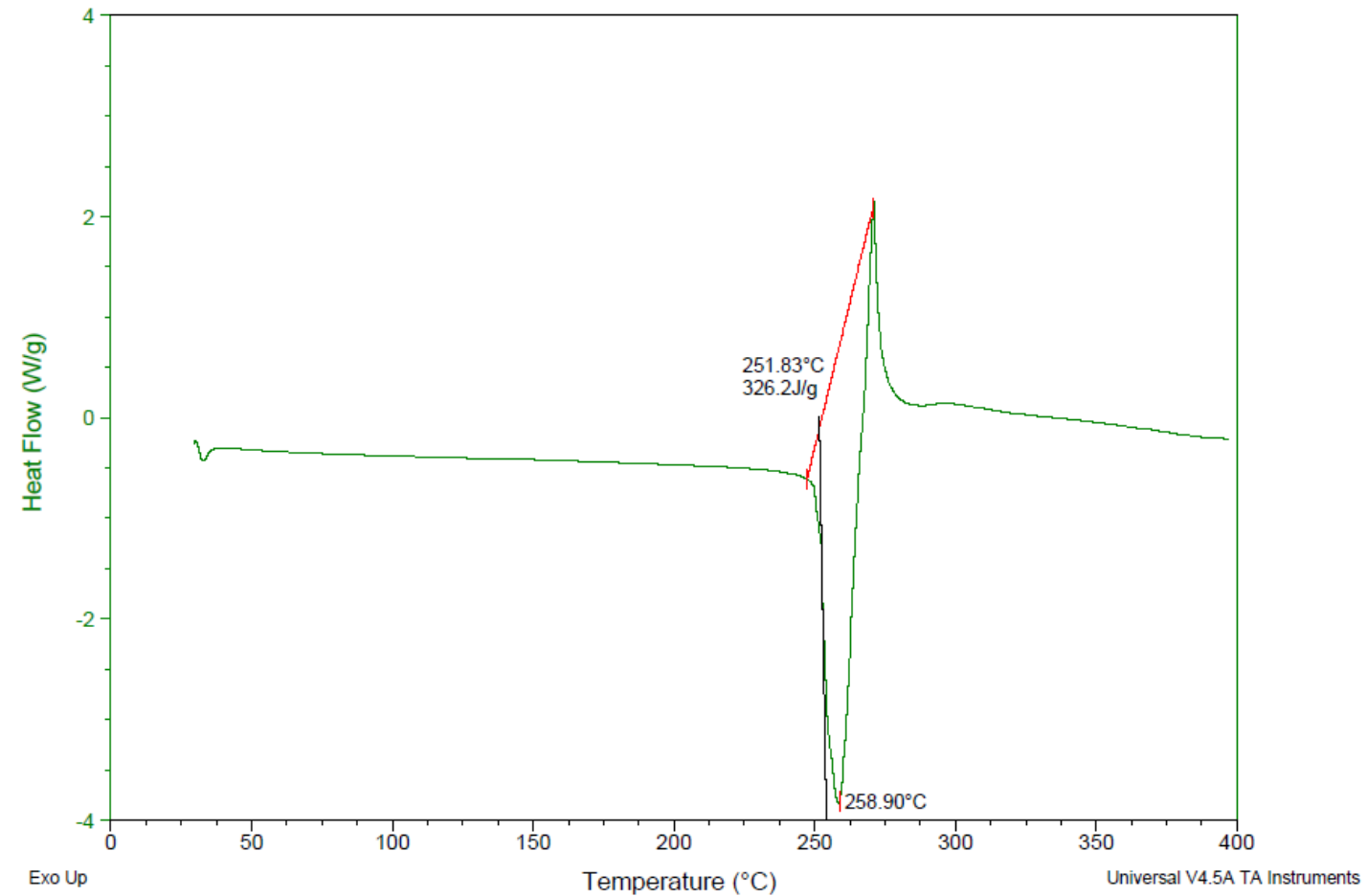


DSC Results – Starting Materials

Sample: Sample 8 Test 2
Size: 15.5000 mg
Method: Polyimides
Comment: Sample 8 Test 2

DSC

File: C:\...13-20-2017\Sample 8 Test 2
Operator: Jackson
Run Date: 23-Mar-2017 09:39
Instrument: DSC Q20 V24.11 Build 124

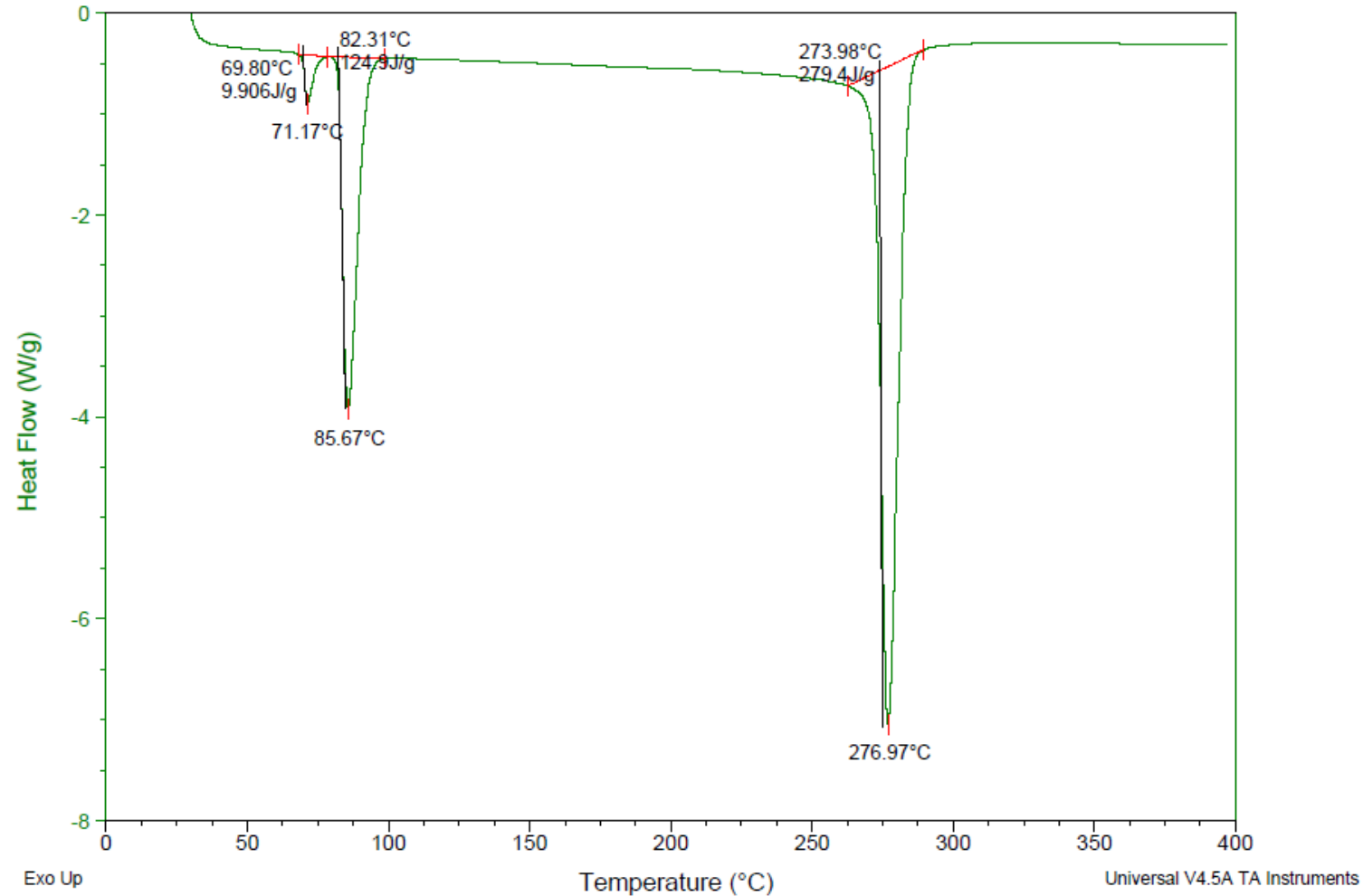


DSC Results – Starting Materials

Sample: Sample TC Test 1
Size: 13.6000 mg
Method: Polyimides
Comment: Sample TC Test 1

DSC

File: C:\...13-20-2017\Sample TC Test 1
Operator: Jackson
Run Date: 23-Mar-2017 20:14
Instrument: DSC Q20 V24.11 Build 124



DSC Results – Polymeric Materials

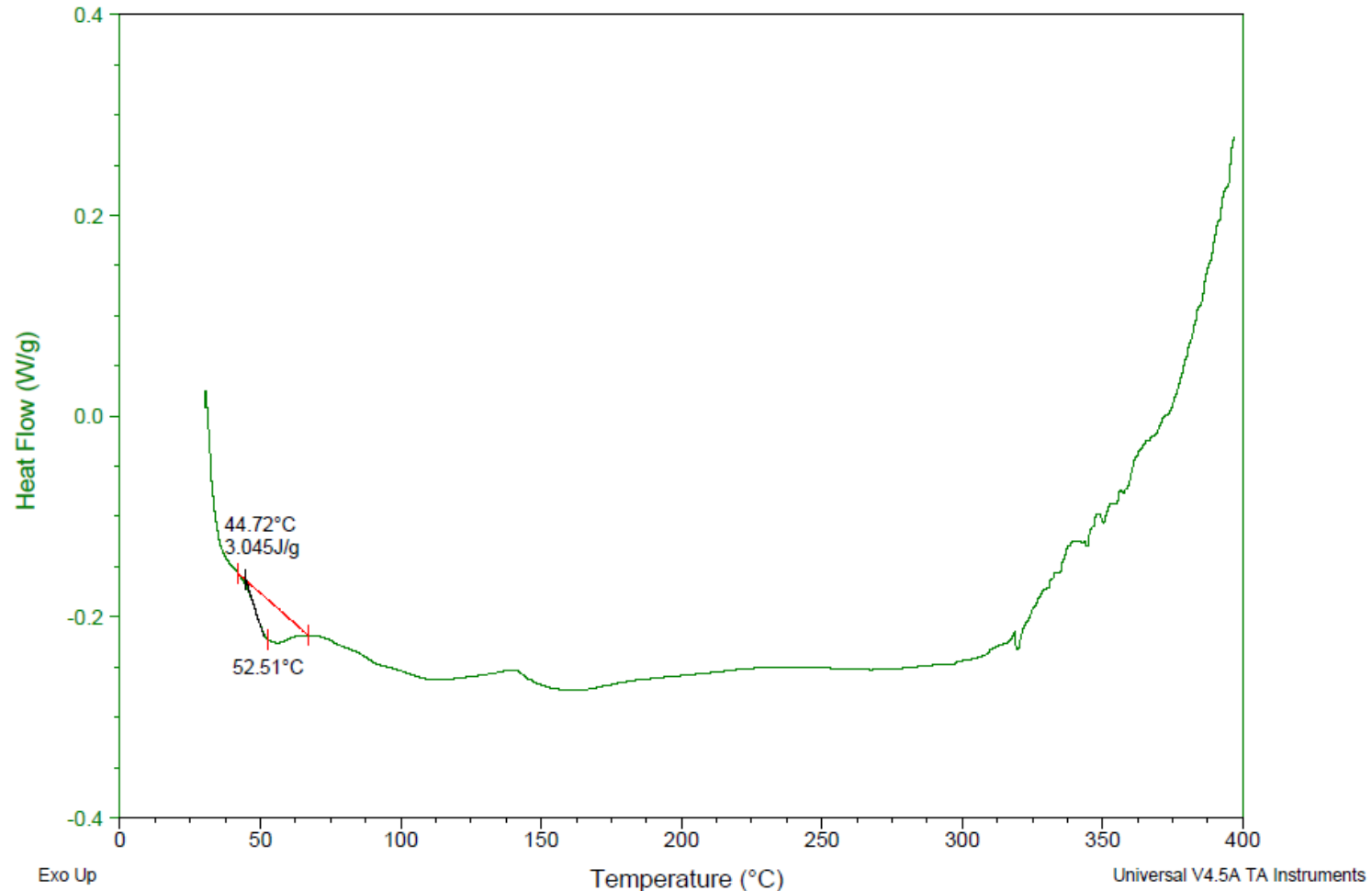
	TC	6FDA	6FDA-Meta	6FDA-Para	PMDA-API-P-XYL	TC-API-M-XYL	6FDA-Starting Mat'L	BPADA-APT-P-XYL
Endotherm #1	67.62 ± 0.36	244.25 ± 0.12	101.21 ± 6.75	80.14 ± 9.98	166.26 ± 8.61	139.16 ± 3.97	244.47 ± 0.05	129.37 ± 5.21
Heat of Fusion #1	9.35 ± 0.63	104.8 ± 4.11	4.90 ± 0.51	50.57 ± 5.12	21.51 ± 0.61	5.86 ± 1.29	98.94 ± 9.80	20.62 ± 8.12
Melting Point #1	69.94 ± 0.77	246.3 ± 0.16	108.62 ± 7.85	132.58 ± 3.80	193.76 ± 1.15	151.07 ± 5.90	246.63 ± 0.21	142.32 ± 5.35
Endotherm #2	81.70 ± 0.38					321.81 ± 2.46		
Heat of Fusion #2	109.27 ± 6.34					0.28 ± 0.24		
Melting Point #2	85.06 ± 1.67					324.17 ± 4.23		
Endotherm #3						340.96 ± 5.92		
Heat of Fusion #3						0.17 ± 0.08		
Melting Point #3						341.48 ± 5.90		

DSC Results – Polymeric Materials

Sample: 6FDA API Ortho XYL
Size: 9.3000 mg
Method: Polyimides
Comment: 6FDA API Ortho XYL Test 1

DSC

File: C:\...19-7-2017\6FDA API Ortho XYL Test 1
Operator: Jackson
Run Date: 11-Sep-2017 12:20
Instrument: DSC Q20 V24.11 Build 124

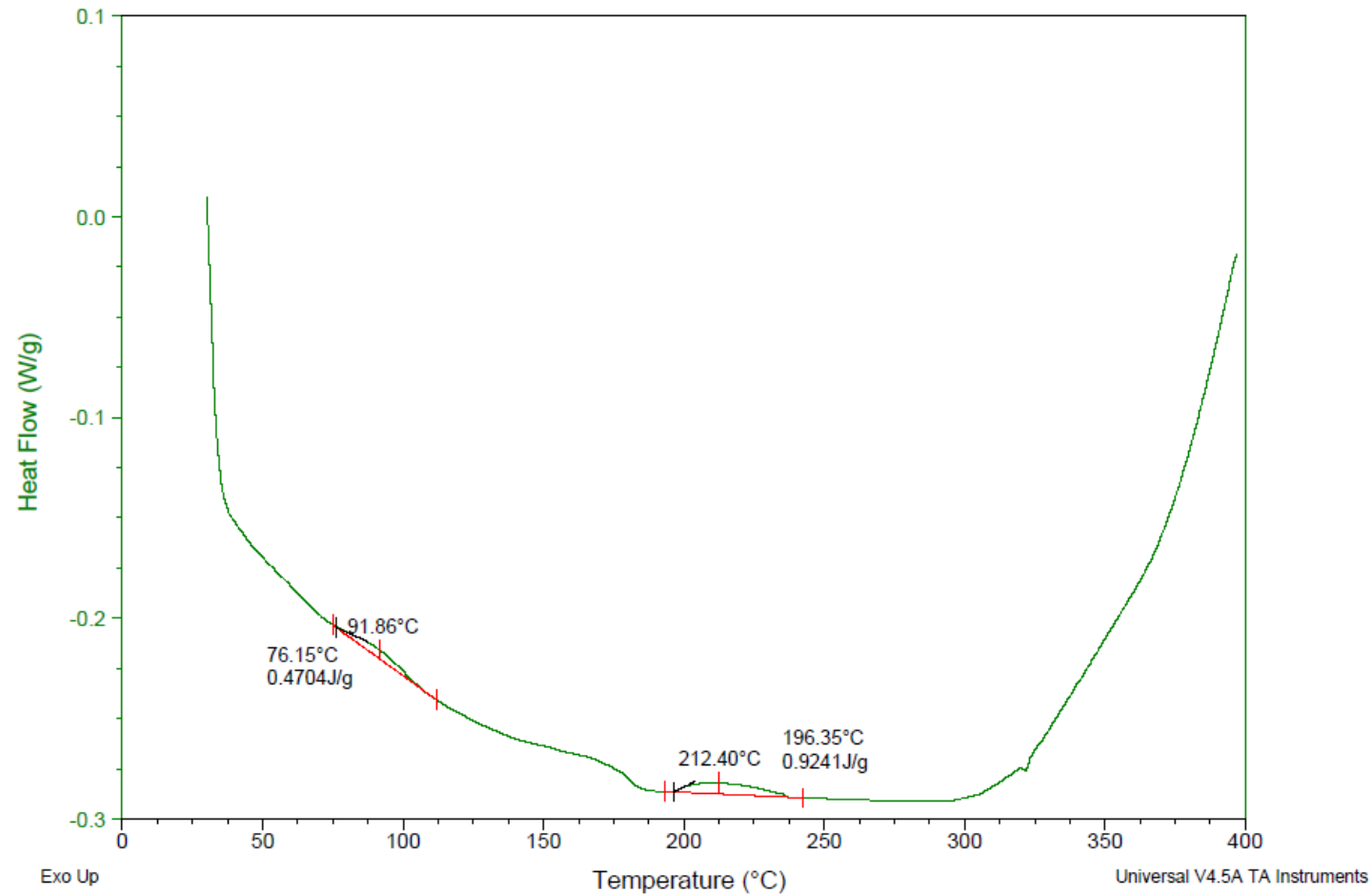


DSC Results – Polymeric Materials

Sample: 6FDA T3A Meta XYL
Size: 8.6000 mg
Method: Polyimides
Comment: 6FDA T3A Meta XYL Test 2

DSC

File: C:\...9-7-2017\6FDA T3A Meta XYL Test 2
Operator: Jackson
Run Date: 08-Sep-2017 08:21
Instrument: DSC Q20 V24.11 Build 124

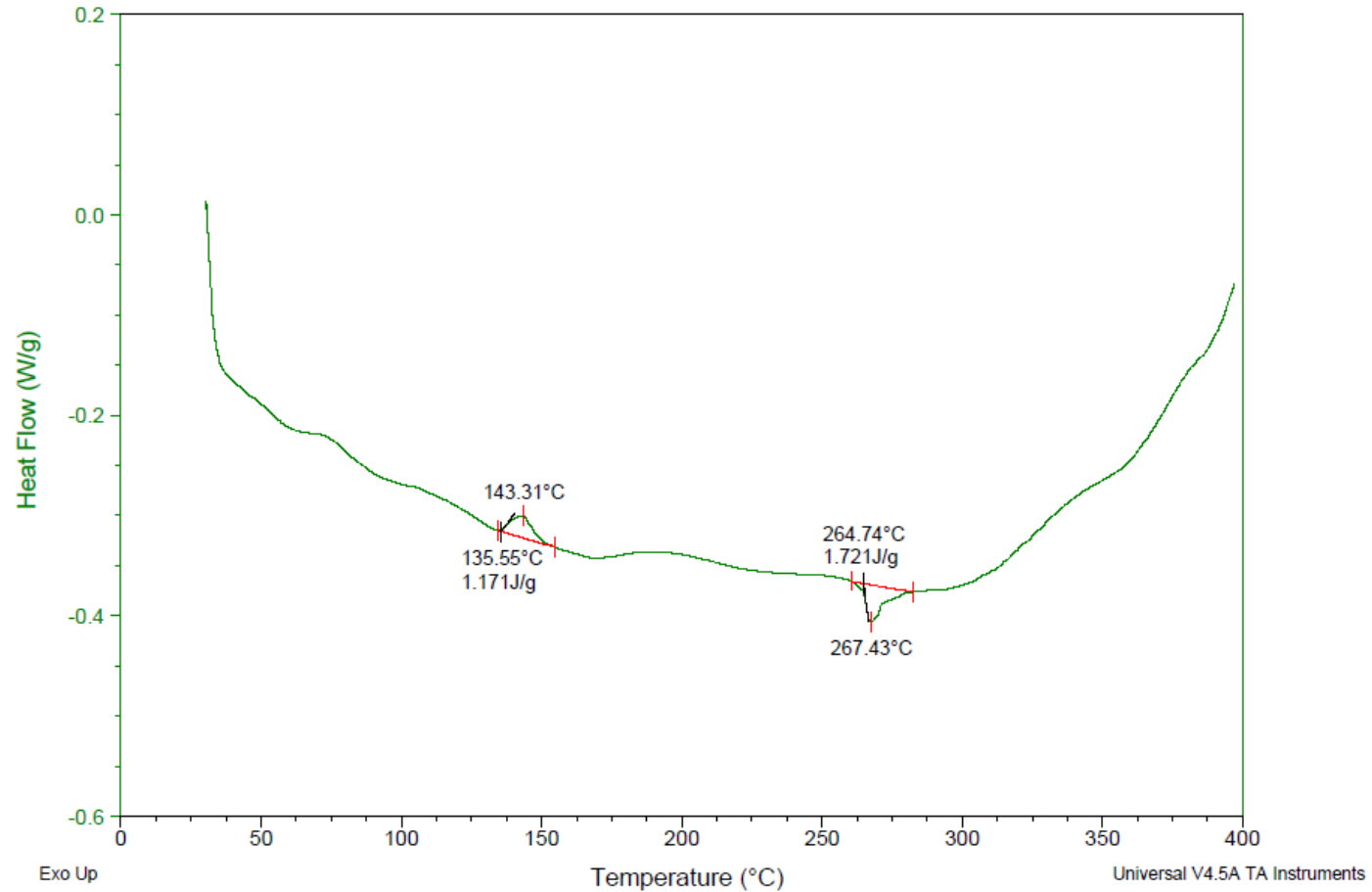


DSC Results – Polymeric Materials

Sample: 6FDA I3A Para XYL
Size: 10.4000 mg
Method: Polyimides
Comment: 6FDA I3A Para XYL Test 1

DSC

File: C:\...19-7-2017\6FDA I3A Para XYL Test 1
Operator: Jackson
Run Date: 08-Sep-2017 11:33
Instrument: DSC Q20 V24.11 Build 124

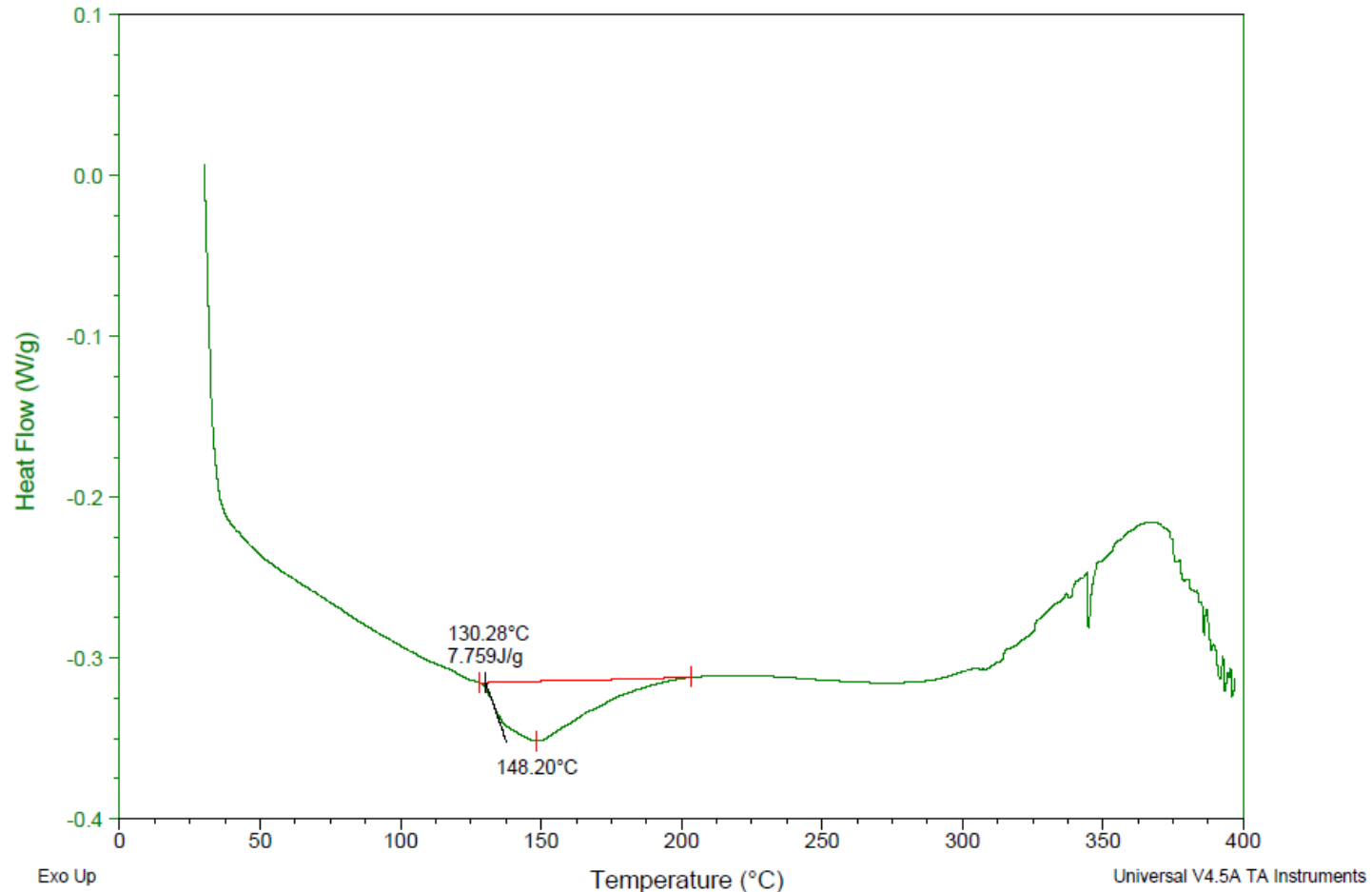


DSC Results – Polymeric Materials

Sample: IC API Ortho XYL
Size: 8.9000 mg
Method: Polyimides
Comment: IC API Ortho Test 1

DSC

File: C:\...19-7-2017\IC API Ortho Test 1
Operator: Jackson
Run Date: 14-Sep-2017 07:53
Instrument: DSC Q20 V24.11 Build 124

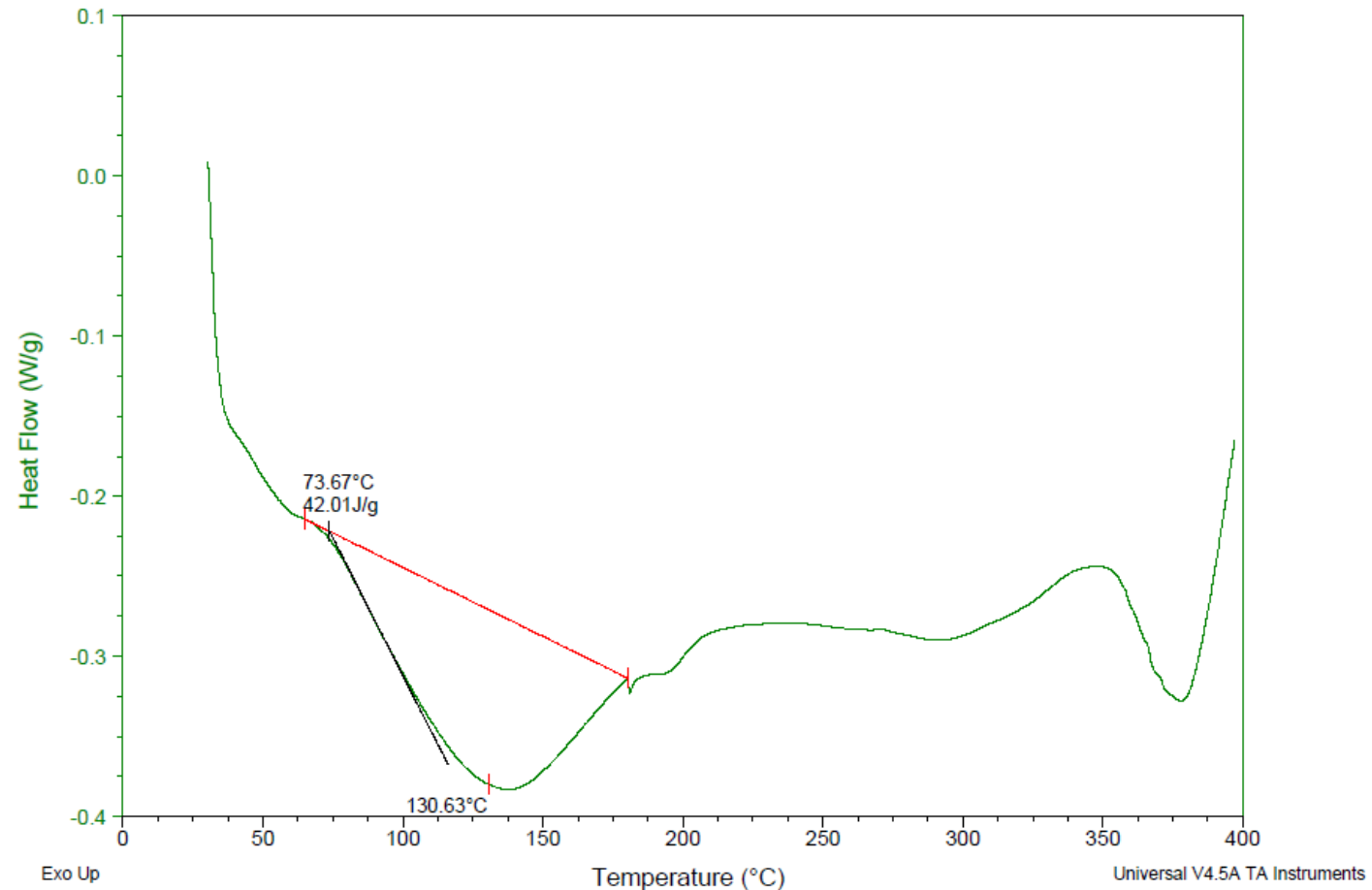


DSC Results – Polymeric Materials

Sample: IC I3A Meta XYL
Size: 7.5000 mg
Method: Polyimides
Comment: IC I3A Meta XYL Test 1

DSC

File: C:\...9-7-2017\IC I3A Meta XYL Test 1
Operator: Jackson
Run Date: 11-Sep-2017 08:11
Instrument: DSC Q20 V24.11 Build 124

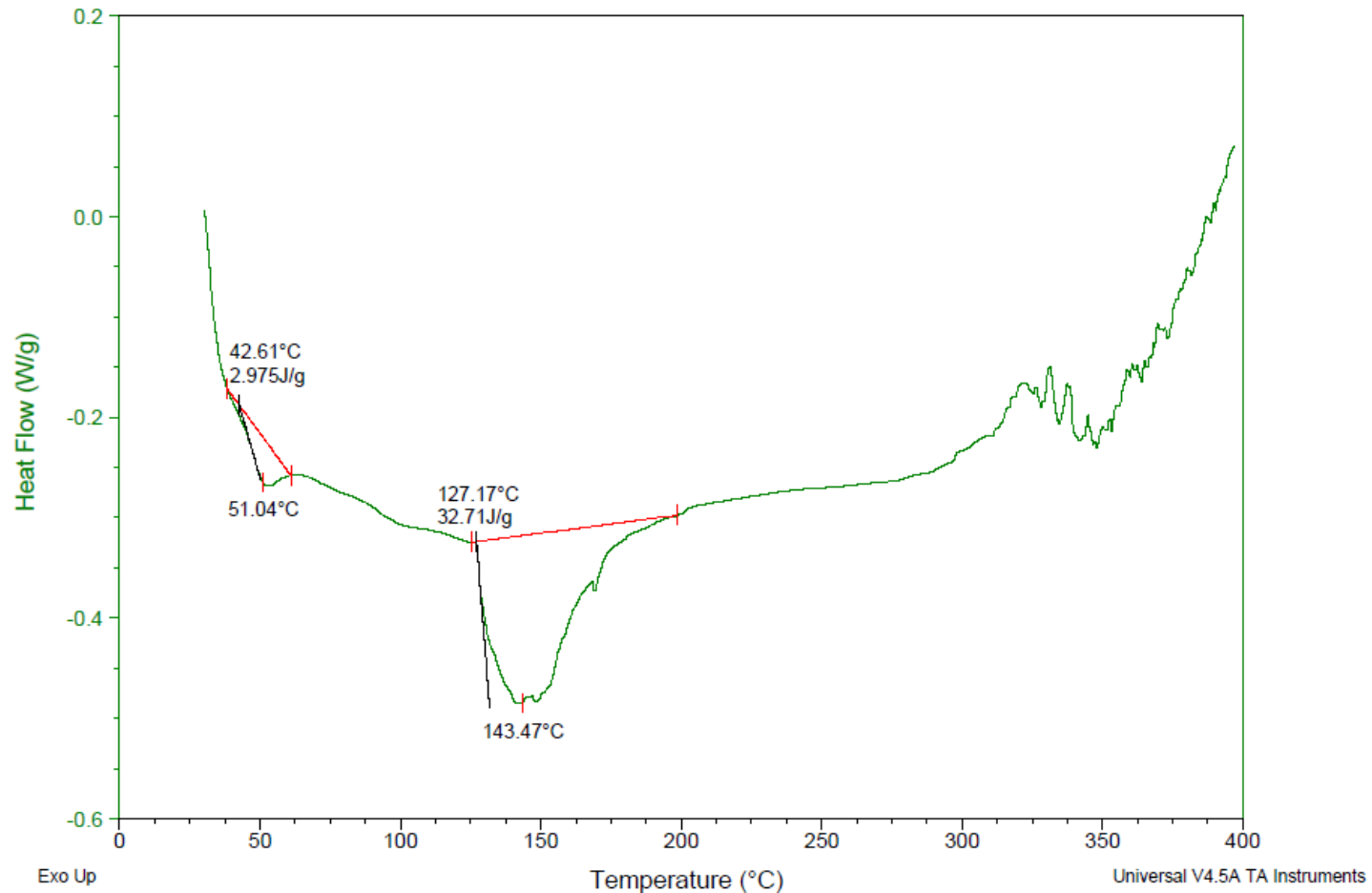


DSC Results – Polymeric Materials

Sample: PDMA XPI Ortho XYL
Size: 11.4000 mg
Method: Polyimides
Comment: PDMA XPI Ortho Test 1

DSC

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Operator: Jackson
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Instrument: DSC Q20 V24.11 Build 124

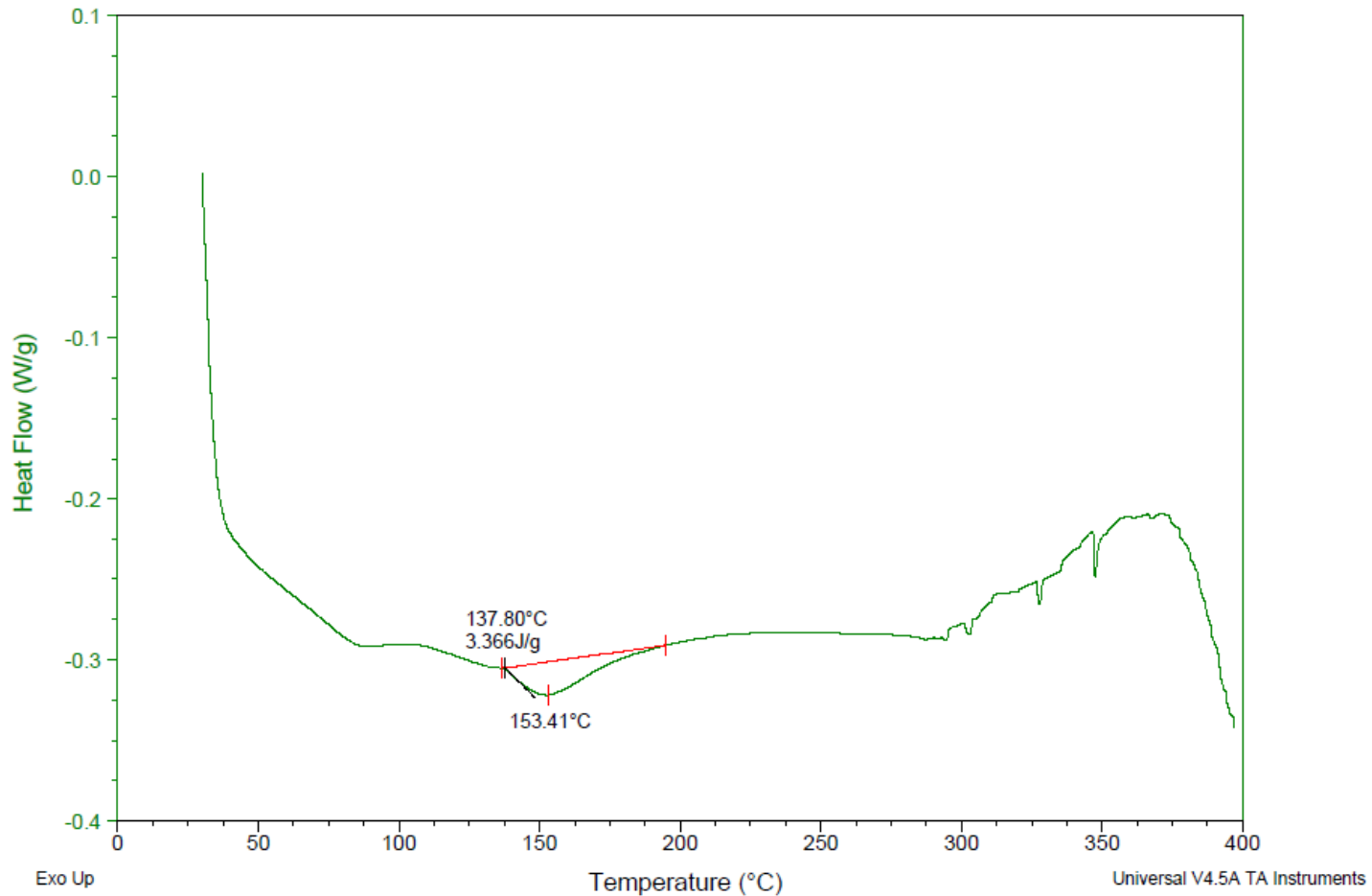


DSC Results – Polymeric Materials

Sample: TC API Ortho XYL
Size: 7.4000 mg
Method: Polyimides
Comment: TC API Ortho Test 1

DSC

File: C:\...19-7-2017\TC API Ortho Test 1
Operator: Jackson
Run Date: 13-Sep-2017 11:55
Instrument: DSC Q20 V24.11 Build 124



TG-IR

- Thermogravimetric analysis (TG) follows changes in mass of the sample as a function of temperature and/or time.
- TG gives characteristic information about the composition of the measured sample, in particular the amounts of the various components and their thermal behavior.
- In addition, further measurements are possible such as kinetic analysis of thermal decomposition.
- The identification of gases released directly from the sample or during thermal treatment cannot be performed just by thermal analysis, but coupling a spectroscopic method such as Fourier-Transform-Infrared (FTIR) spectroscopy is an excellent solution.

TG-IR cont.

- IR spectroscopy is a classical technique, which depends upon the interaction of infrared radiation with the vibrating dipole moments of molecules.
- It gives, with the exception of homonuclear diatomics and noble gases, a characteristic spectrum for each substance.
- TG-FTIR is useful for a wide range of applications, including:
 - Outgassing of Materials
 - Detection of Residues
 - Analysis of Additives
 - Analysis of Aging Processes
 - Competitive Analysis
 - Characterization of Natural and Raw Materials
 - Desorption Behavior
 - Analysis of Synthesis Processes
 - Analysis of Decomposition Processes

TG-IR Data

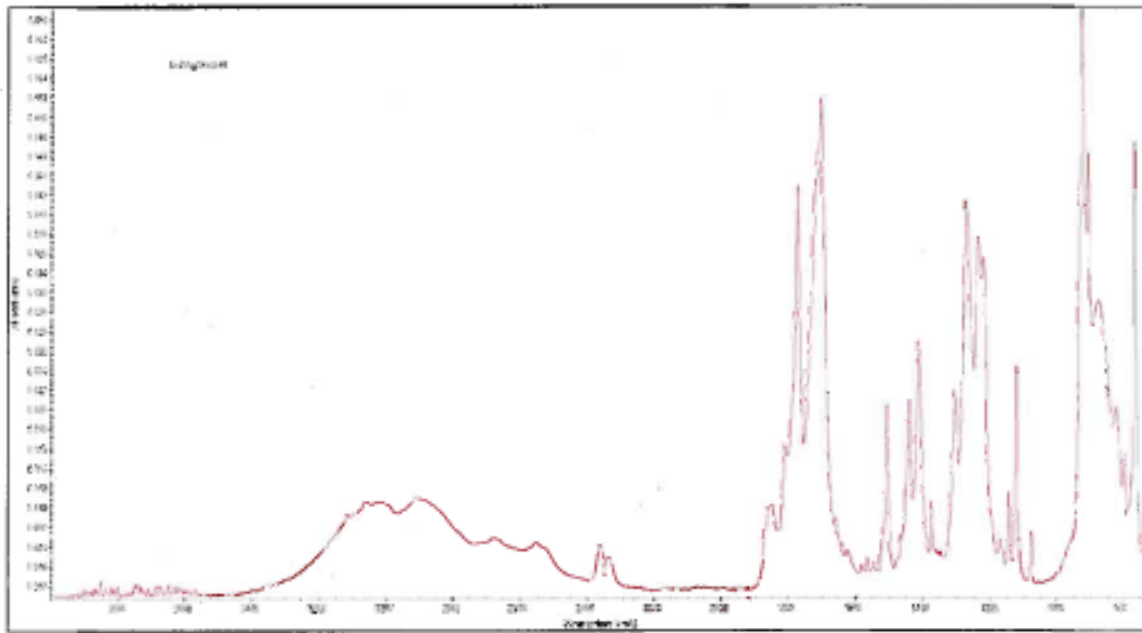


Figure 1. Infrared Spectrum of Building Block #1

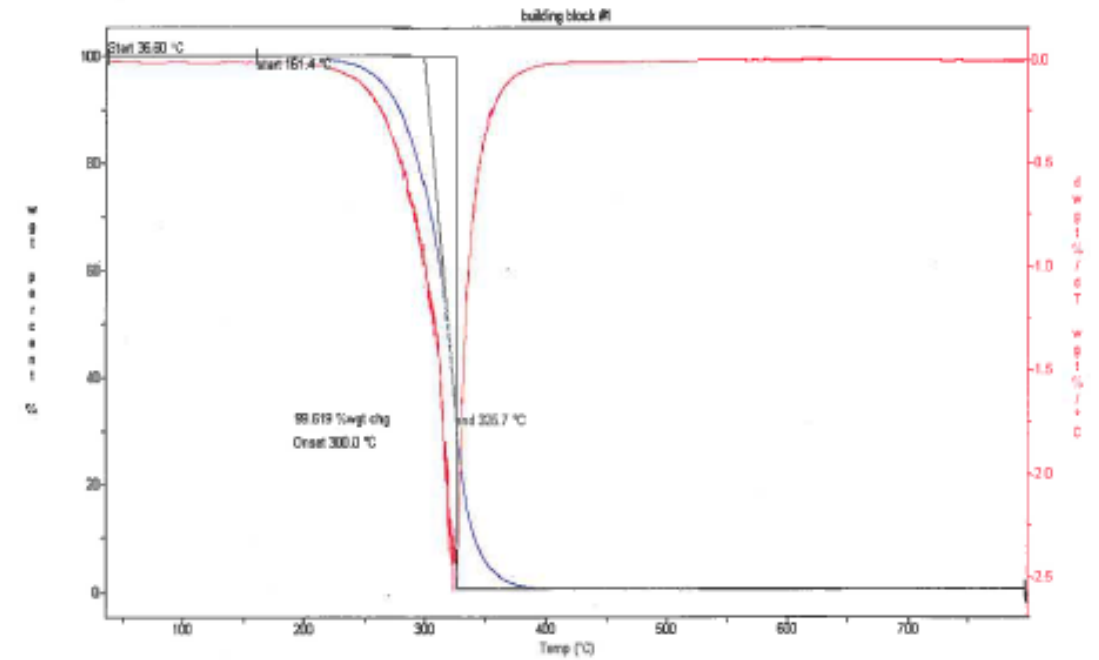


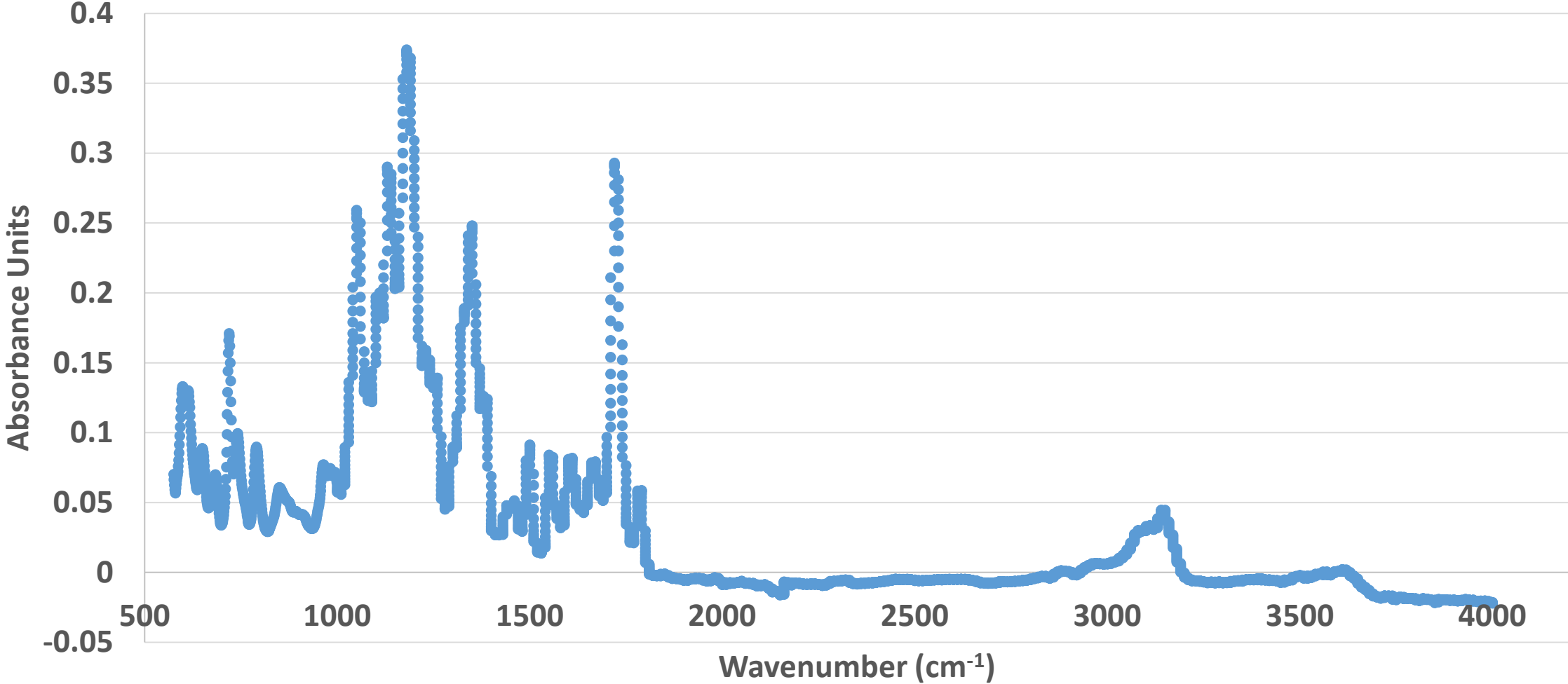
Figure 2. TGA Profile of Building Block #1

FTIR Experimental Method

- ATR module with germanium crystal and pressure device (thunderdome)
 - 64 scans
 - 4 resolution

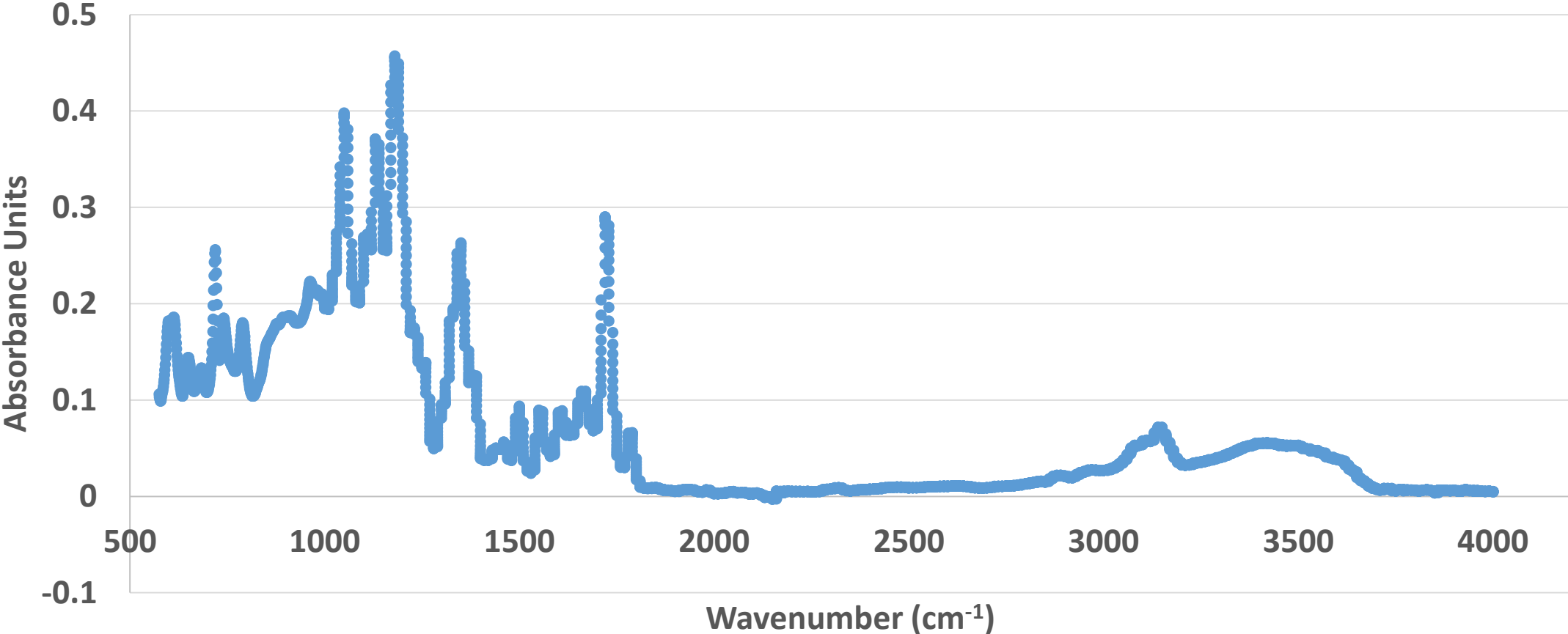
FTIR Data – Condensed Stage

6FDA I3A Meta XYL



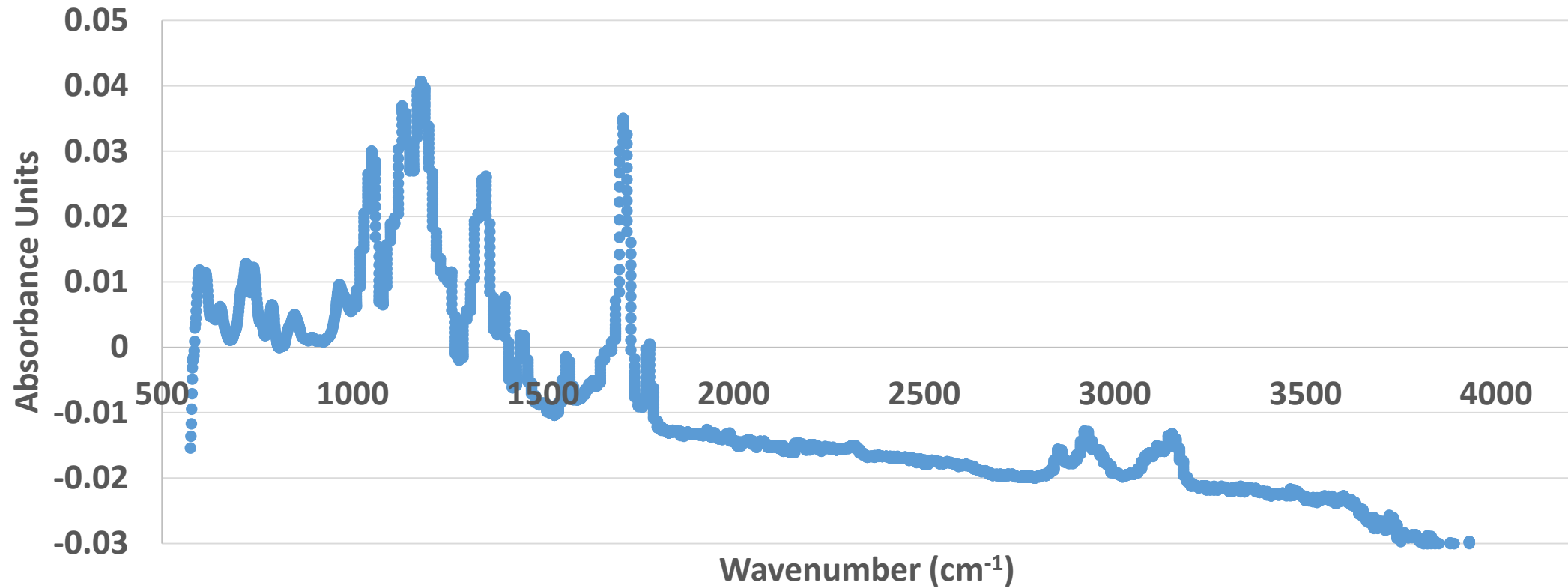
FTIR Data – Condensed Stage

6FDA I3A Para XYL

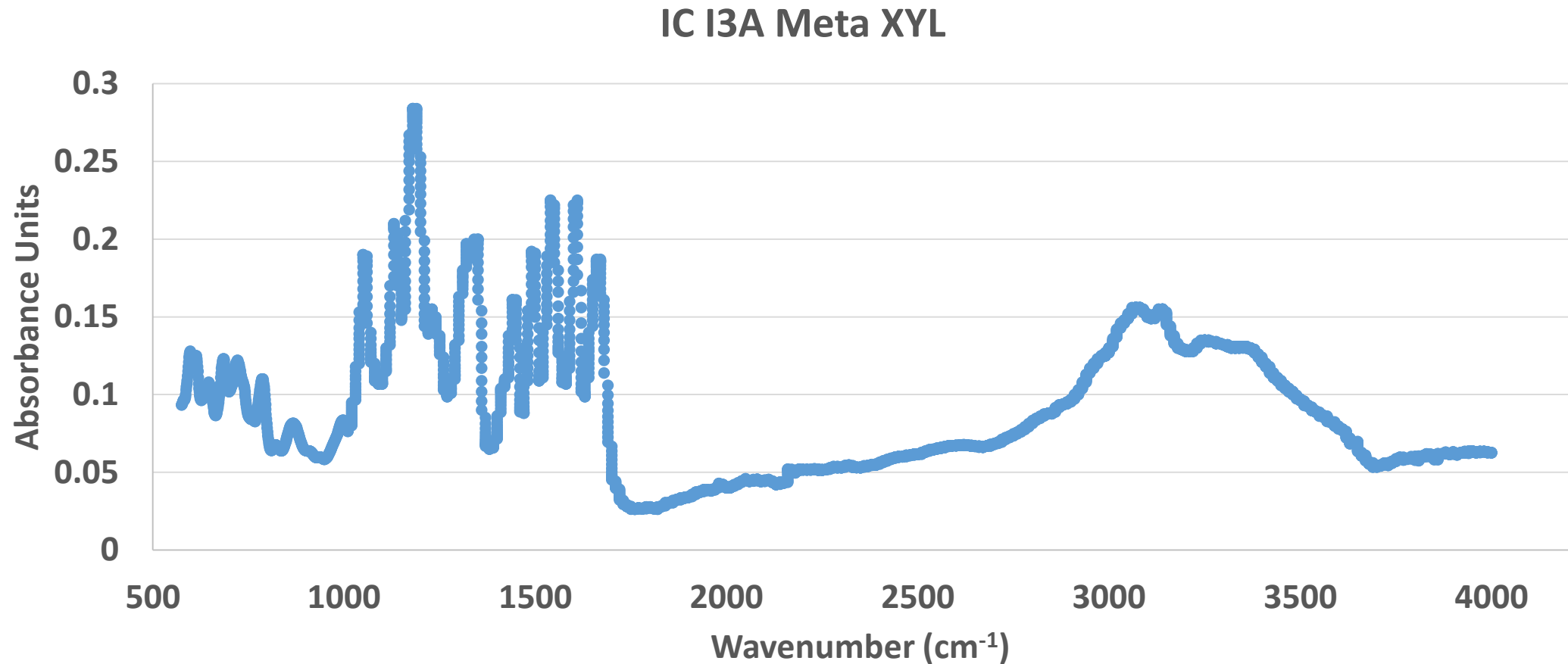


FTIR Data – Condensed Stage

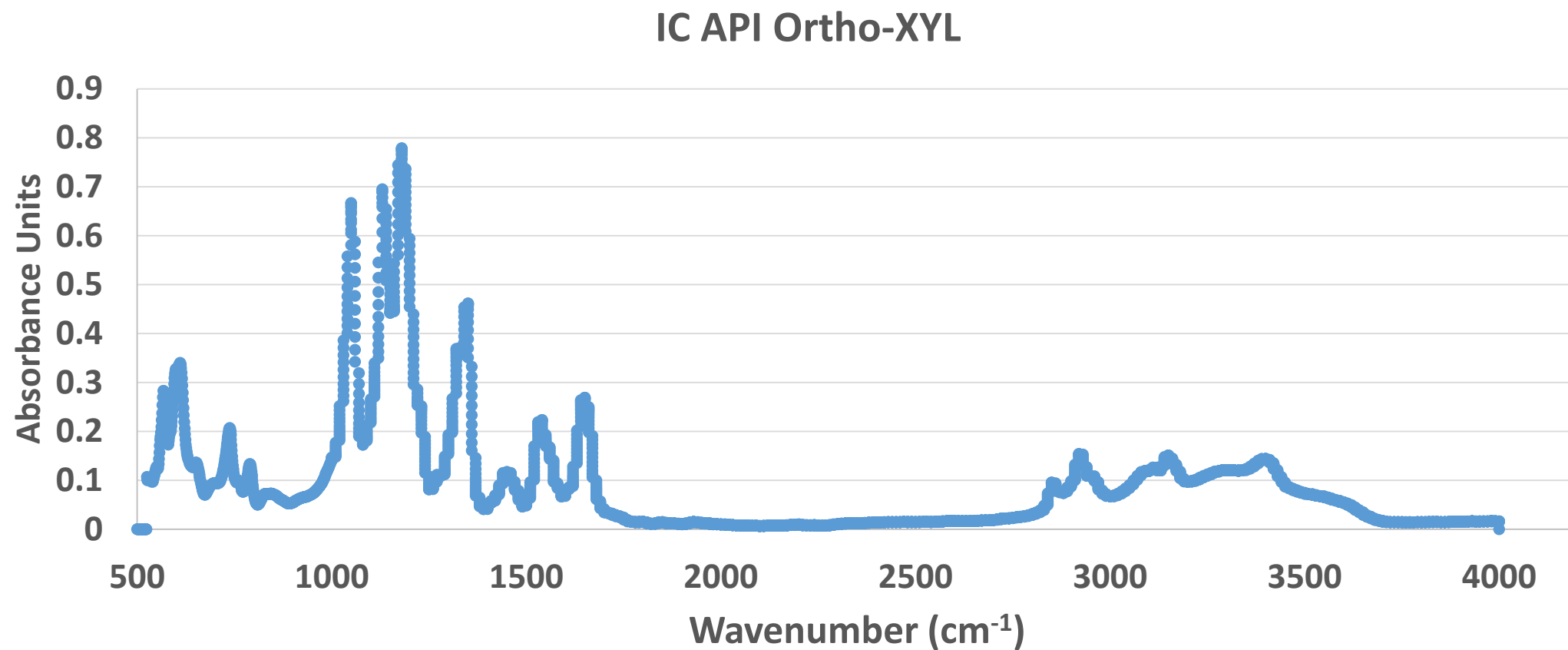
6FDA API Ortho-XYL



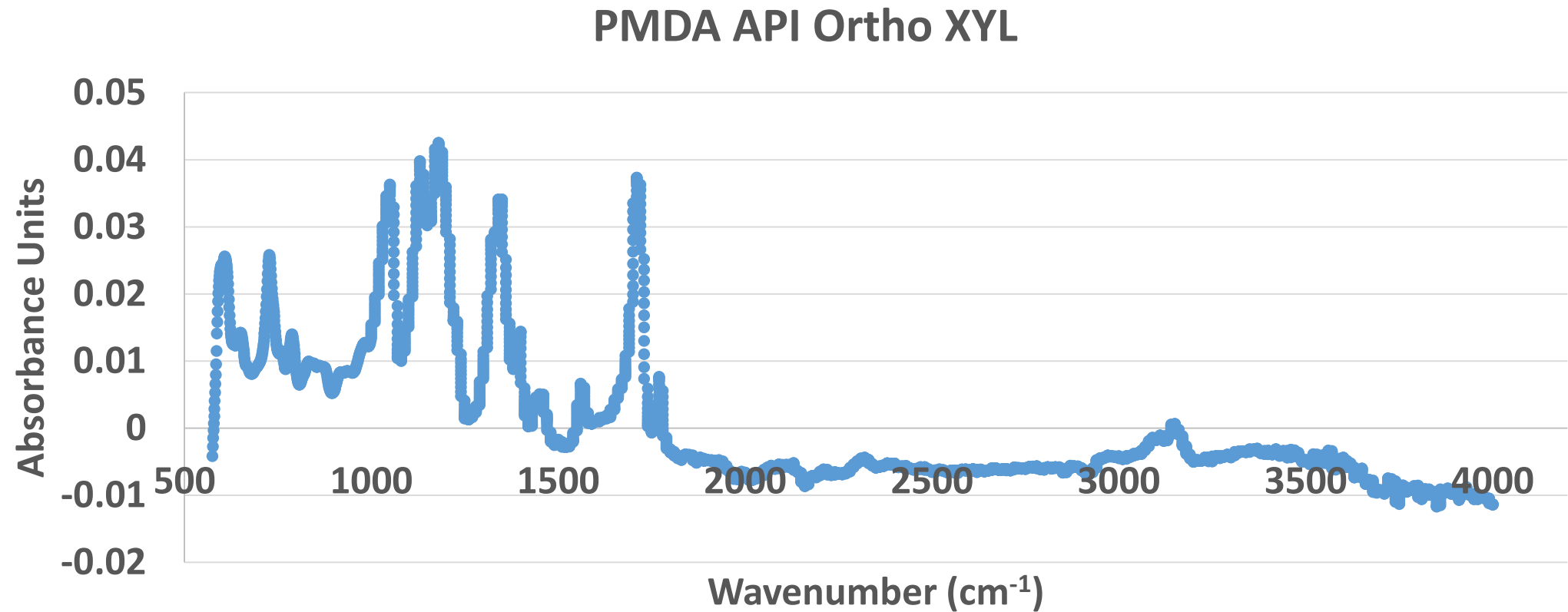
FTIR Data – Condensed Stage



FTIR Data – Condensed Stage

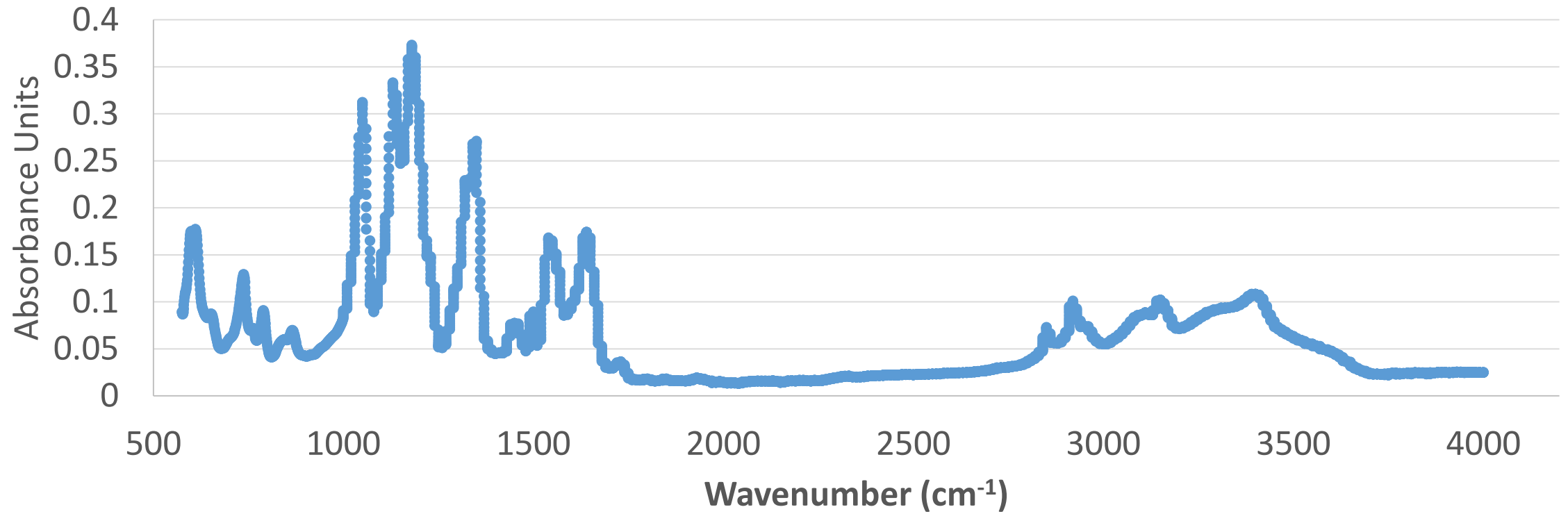


FTIR Data – Condensed Stage



FTIR Data – Condensed Stage

TC API Ortho XYL



Molecular Modeling

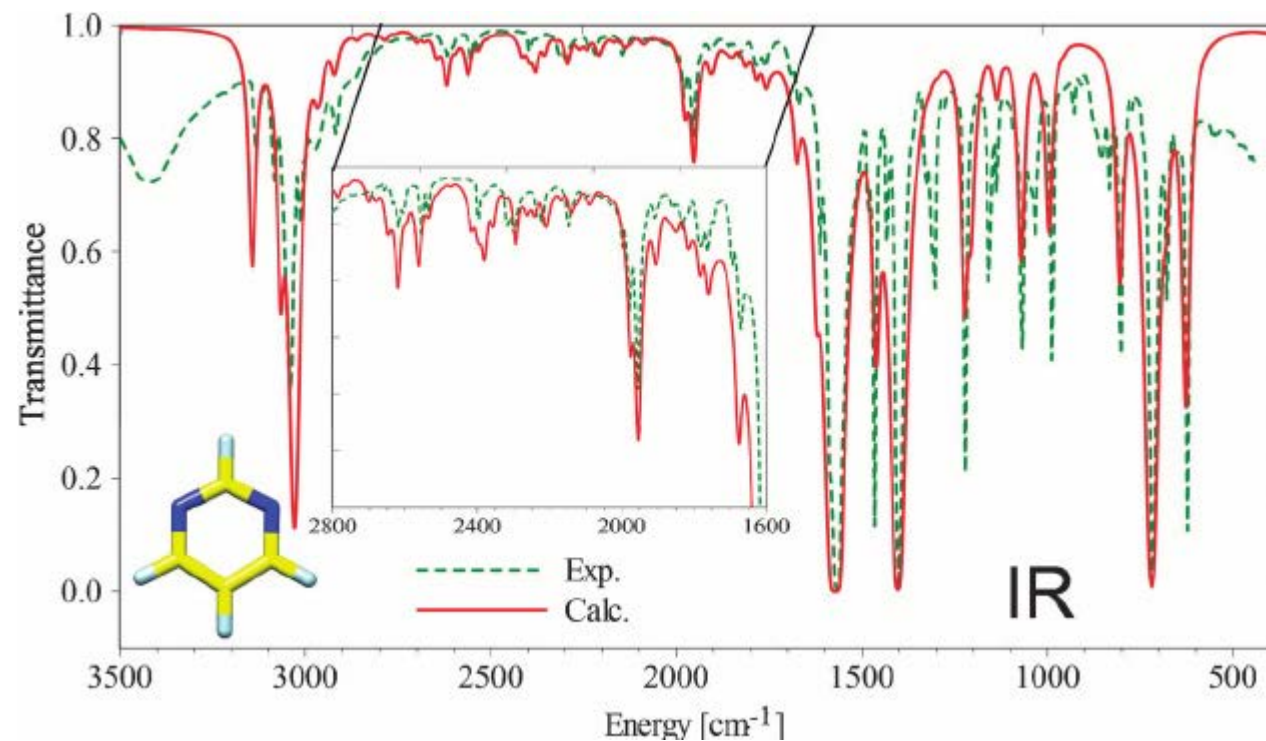
- Properties of ionic polyimides not strictly dependent on bulk structure are calculated using Gaussian '16:
 - Heats of formation
 - Heats of solvation
 - Heats of reaction (isodesmic series)
 - Infrared and Raman spectra
 - Charge transfer (conductivity)
- Bulk property estimation using molecular dynamics
 - Glass transition temp
 - Others...

Ab Initio Calculations

- Heats of formation are calculated using a Gaussian-3 (G3) formulation, which isolates sources of error in individual methods and derives total energy from the ensemble of energies:
 - Equilibrium structure optimized at HF/6-31G(*d*)
 - Zero-point energy calculated using harmonic frequencies scaled for 6-31G(*d*) basis
 - Geometry optimized at MP2/6-31G(*d*), single-point at MP4/6-31G(*d*); used in subsequent single-point calculations:
 - **Diffuse correction: MP4/6-31+G(*d*)**
 - **Polarization correction: MP4/6-31G(2*df*,*p*)**
 - **Correlation correction: QCISD(T)/6-31G(*d*)**
 - **Basis correction: “G3Large” basis (3*d* 2*f* 2*df*)++****
 - **Spin-orbit and valence corrections: empirical**
 - Total energy equivalent to QCISD(T)(full)/6-311++G(3*df* 2*df* 2*dp*)

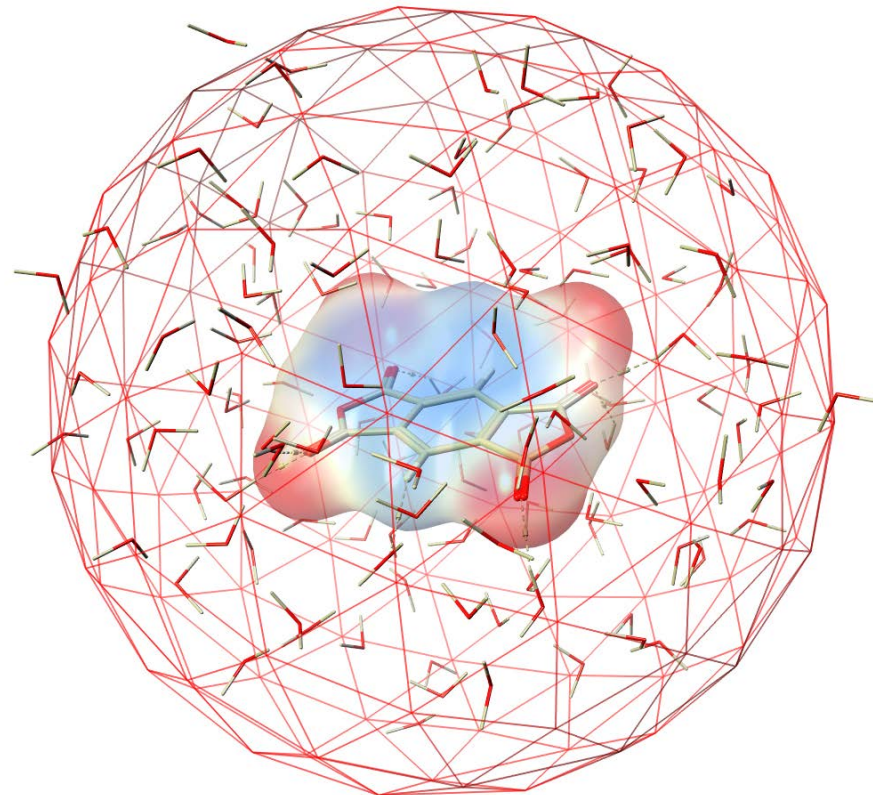
IR & Raman

- Infrared and Raman spectra are calculated from the harmonic vibrational frequencies using medium-range correlation corrected density functional theory:
 - The Minnesota functionals, Mxx; *e.g.* M06, M06-2X
 - The inclusion of Grimme's correction into other



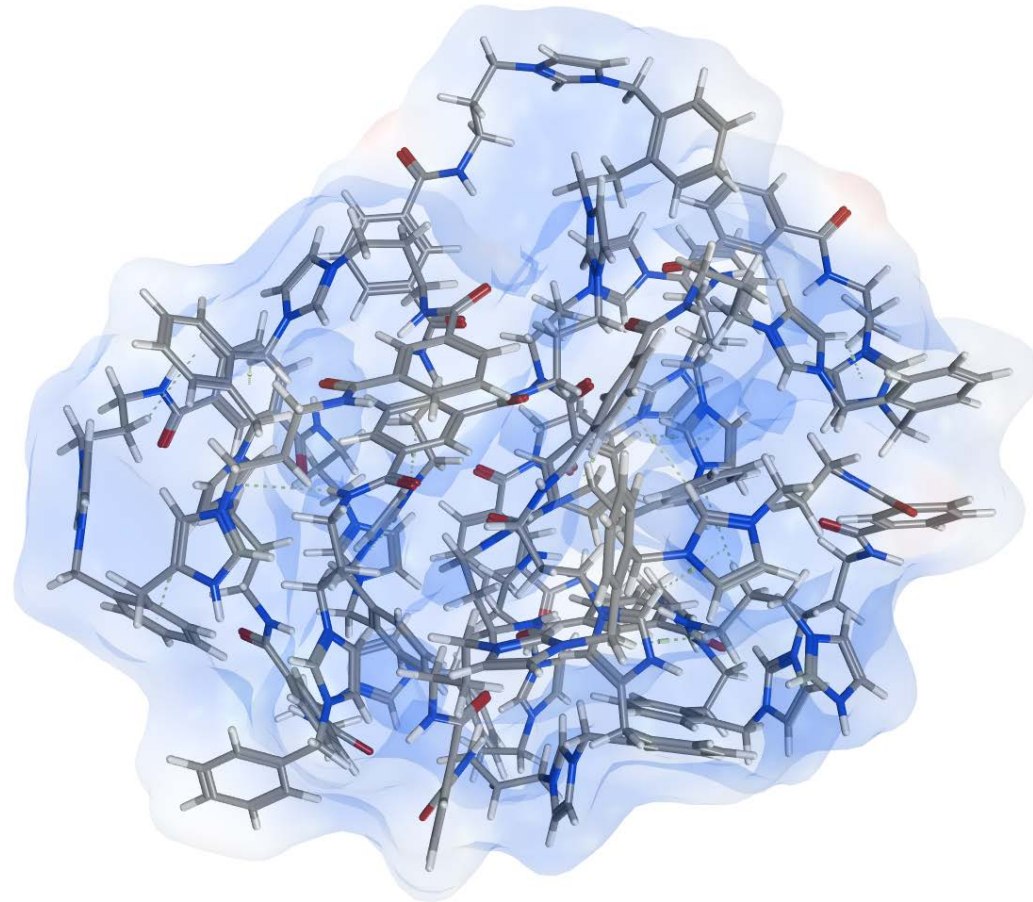
Solvation

- Heats of solvation are determined using self-consistent reaction field calculations with medium-range correlation corrected density functional theory with the SMD method in G16
 - The Minnesota functionals, Mxx; *e.g.* M06, M06-2X



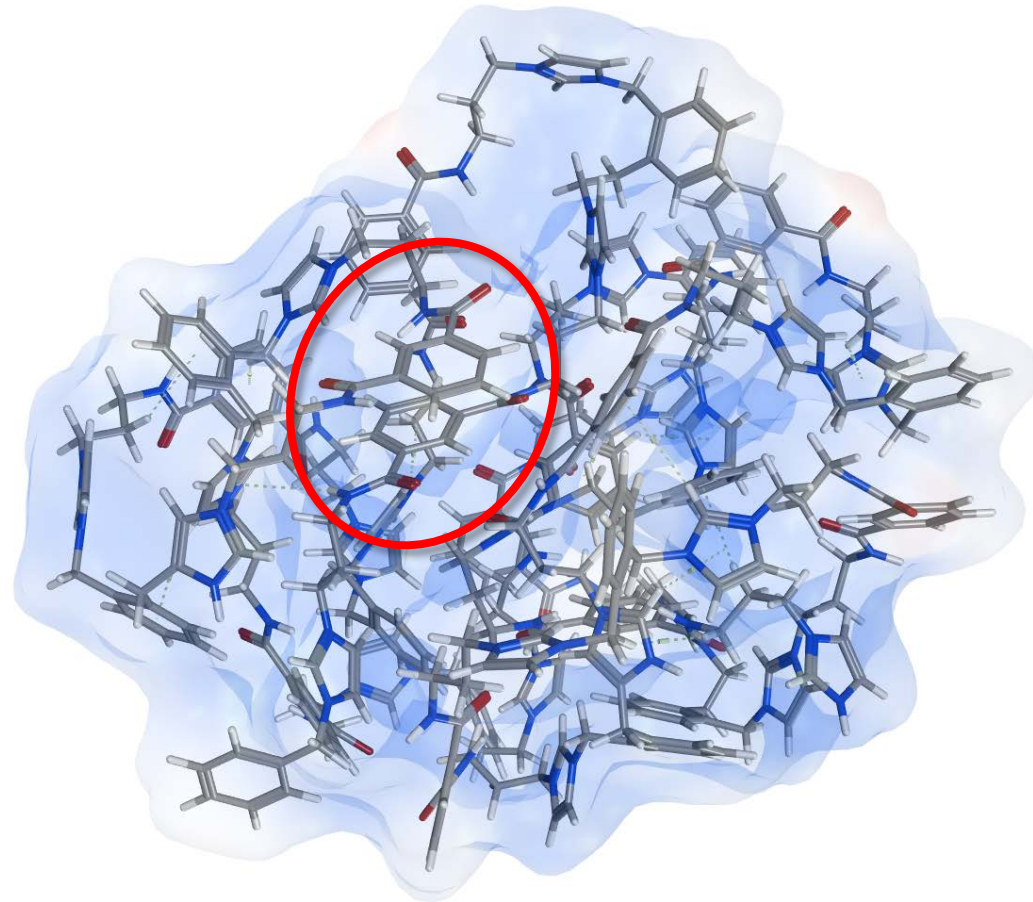
Charge Transfer

- Conductive/semiconductive properties may be estimated from monomer polarizabilities and from the calculation of charge transfer in local ring systems using Symmetry-Adapted Perturbation Theory



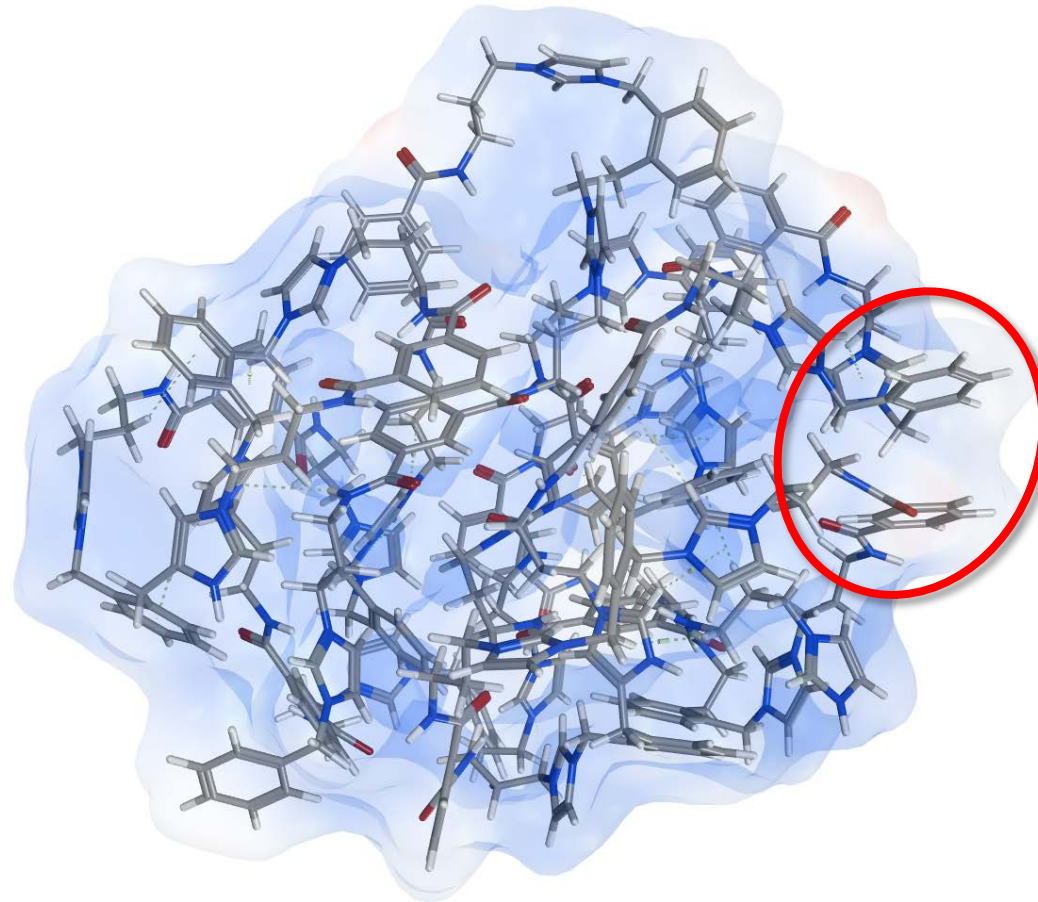
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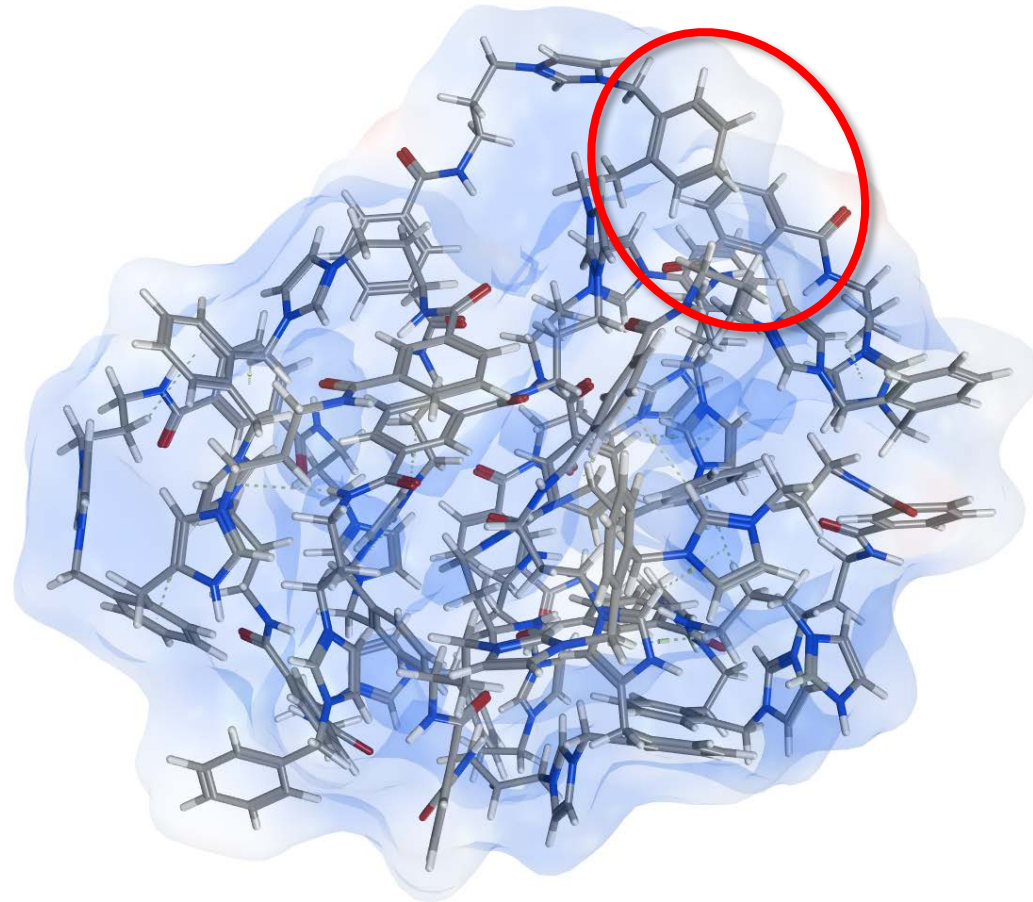
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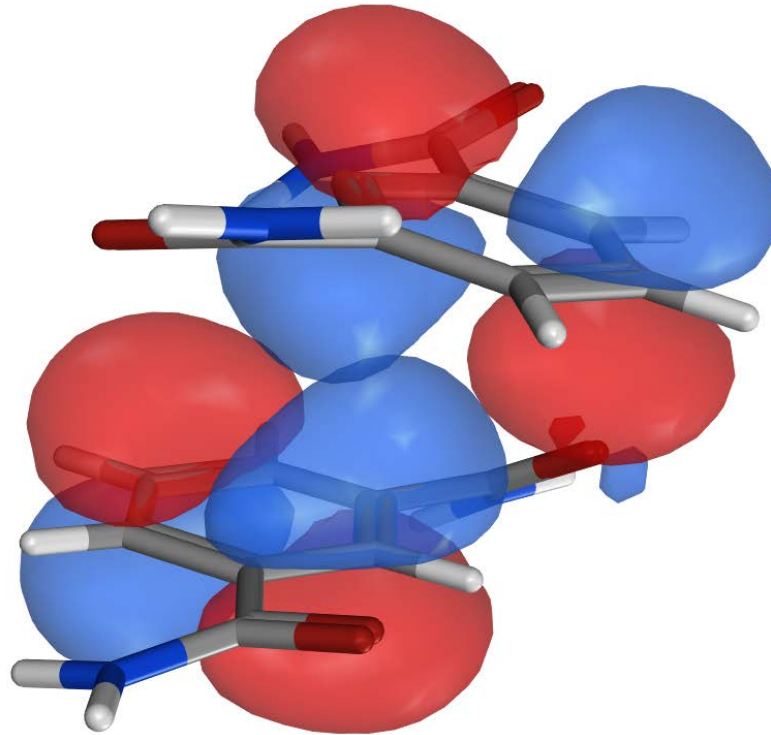
Charge Transfer

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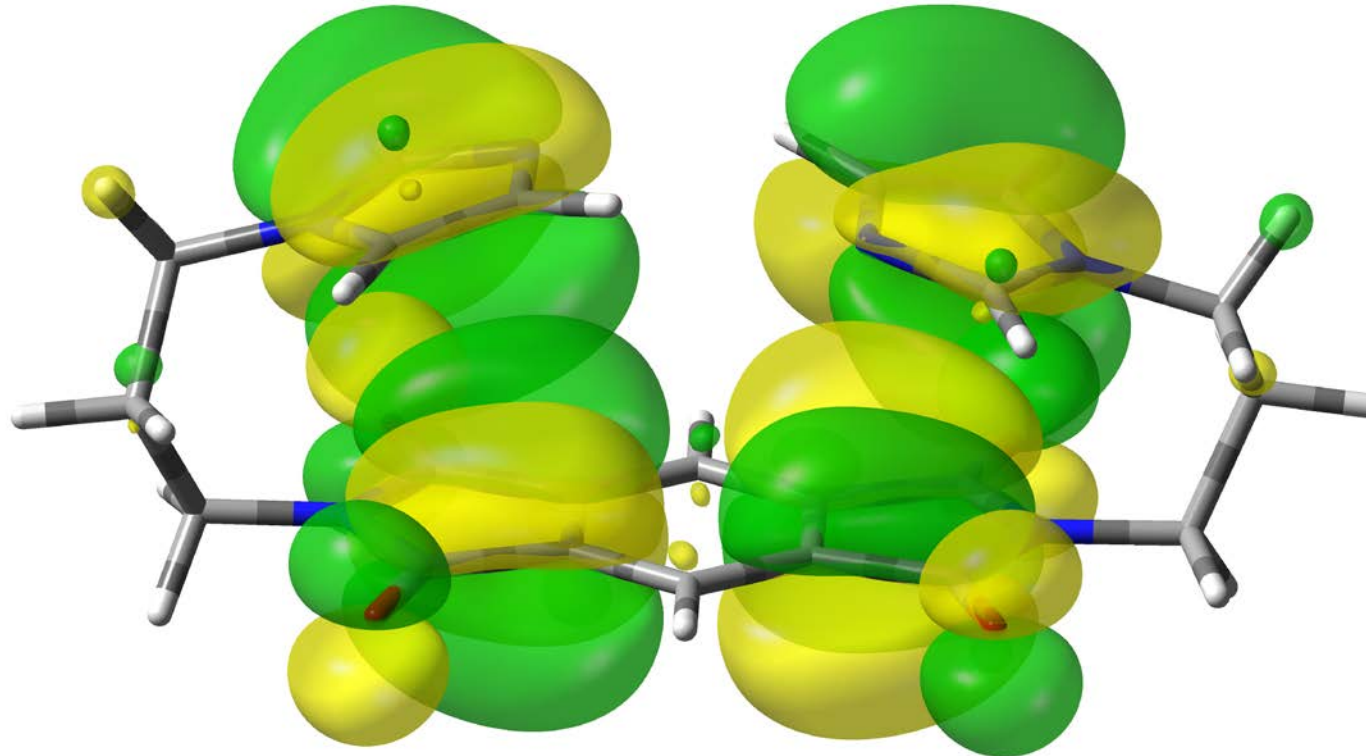
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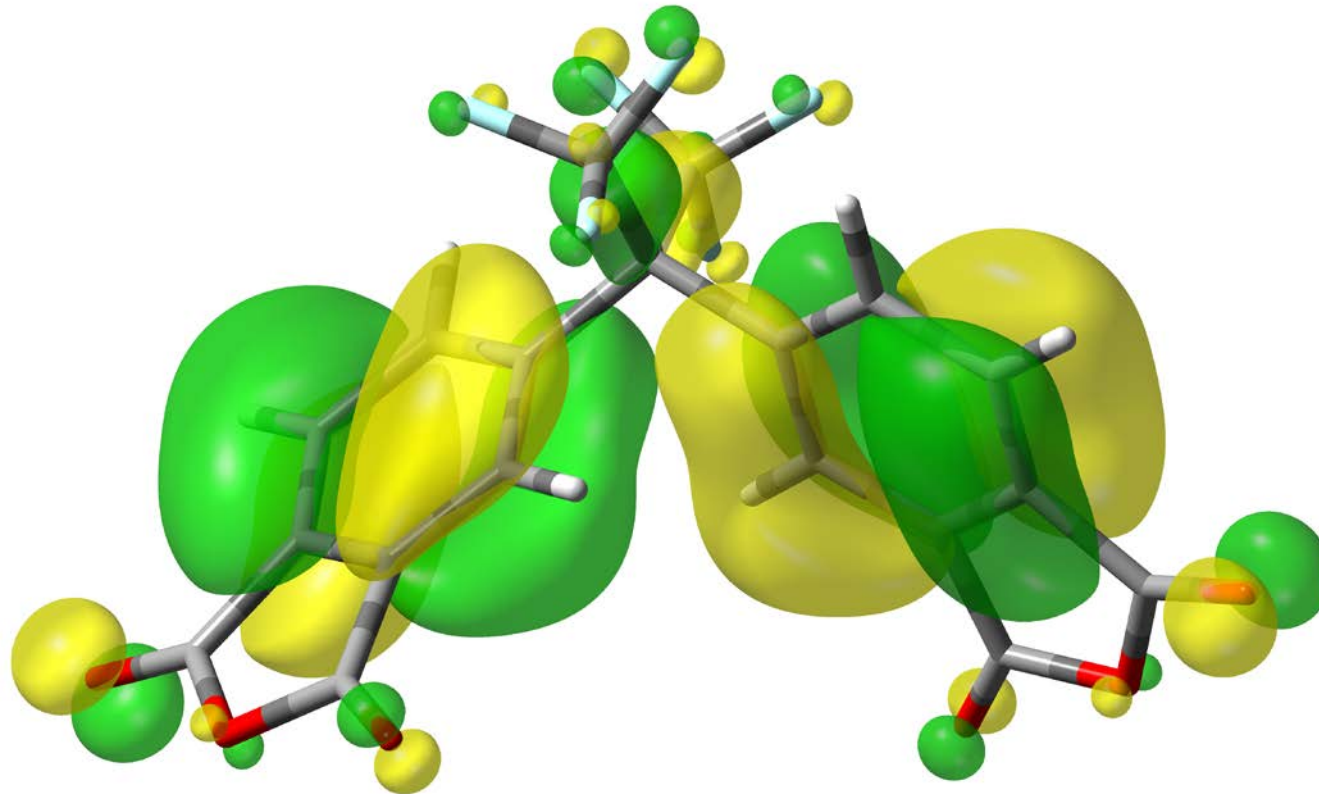
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Glass Transition Temperature

- Glass Transition Temperature (T_g) has been estimated with reasonably small errors for OLED polymers from surface polarizabilities of monomers using quantitative structure-property modelling

$$\begin{aligned} f(T_g)(\mathbf{r}) = & -0.286 \cdot \sqrt{|V(\mathbf{r})|} - 5.091 \times 10^{-2} \cdot V(\mathbf{r}) + 9.633 \times 10^{-3} \cdot [V(\mathbf{r})]^{3/2} \\ & + 6.251 \times 10^{-6} \cdot [V(\mathbf{r})]^3 - 3.745 \times 10^{-3} \cdot EA_L(\mathbf{r}) + 5.833 \cdot [\alpha_L(\mathbf{r})]^{5/2} \\ & - 7.761 \times 10^{-4} \cdot V(\mathbf{r}) \cdot EA_L(\mathbf{r}) - 2.385 \times 10^{-2} \cdot [V(\mathbf{r}) \cdot \alpha_L(\mathbf{r})]^{3/2} \\ & - 3.135 \times 10^{-5} \cdot [V(\mathbf{r}) \cdot \alpha_L(\mathbf{r})]^3 \\ & + 5.192 \times 10^{-20} \cdot [V(\mathbf{r}) \cdot IE_L(\mathbf{r}) \cdot EA_L(\mathbf{r})]^3 \\ & + 2.521 \times 10^{-13} \cdot [V(\mathbf{r}) \cdot IE_L(\mathbf{r}) \cdot \alpha_L(\mathbf{r})]^3 \\ & + 1.843 \times 10^{-10} \cdot [V(\mathbf{r}) \cdot EA_L(\mathbf{r}) \cdot \alpha_L(\mathbf{r})]^3 + 252.25 \end{aligned}$$

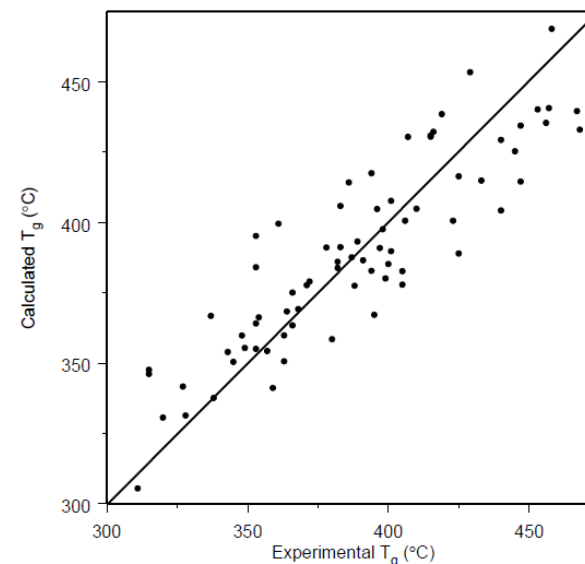
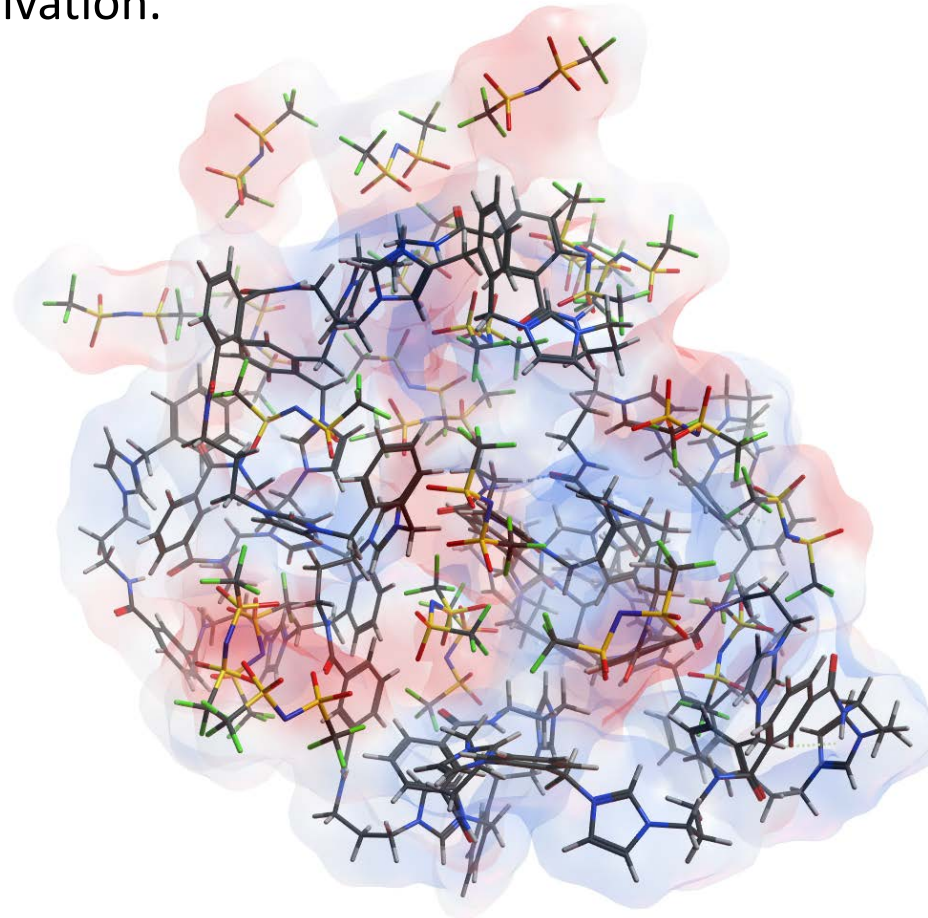


Figure 2.24 Surface-integral model for glass transition temperature using COSMO-optimized structures:
MUE= 15.3, RMSD= 18.7, $r^2= 0.779$, $r^2_{cv}=0.491$.

Glass Transition Temperature

- A gas solubility study of ionic polyimide oligomers using molecular dynamics (MD) has recently been published. MD may also be used to model bulk properties such as a T_g using either explicit solvation or continuum solvation.



Future Work

- Continue synthesizing different variations of these polyimides
- Characterize these polyimides with different thermal characterization techniques
 - DSC
 - TG-IR
 - FTIR
- Model these polyimides via ab-initio calculations
- Develop filament feedstock materials from these ionic liquids to additively manufacture these materials for aerospace applications

Questions?

