SYNTHESIS AND CHARACTERIZATION OF THE POLYHYDROXYAMIDE/POLYMETHOXYAMIDE FAMILY OF POLYMERS

Arthur J. Gavrin, *Eui-Sang Yoo, Richard J. Farris, E. Bryan Coughlin*

Department of Polymer Science and Engineering,
University of Massachusetts,
Amherst, MA 01003

ABSTRACT: The poly(hydroxy-amide) [PHA] family of polymers possess not only high temperature stability, but also form a more thermally stable polymer (polybenzoxazole) [PBO] during thermal decomposition. The synthesis occurs in solution at low temperature, preventing premature ring cyclization to PBO. The molecular structure was confirmed from ^{1}H-, ^{13}C-NMR, and elemental analysis. One drawback for the highly aromatic PHA is the lack of a softening temperature before the onset of ring closure to PBO. Thus, poly(methoxy-amide) [PMeOA] and random copolymers of PHA and PMeOA have been synthesized and characterized. From microcalorimetry, the peak heat release capacity values for the copolymers is typically higher than that of the pure PHA (while still much lower than most other polymers); however, DSC analysis has shown Tg's to as low as 151°C for the copolymers. Furthermore, TMA experiments of free-standing films containing between 10 and 20wt% of solvent show the ability to lower the softening temperature as much as 70°C, compared to the Tg shown from the DSC. TGA displays a three-step degradation associated with two ring closures to PBO from PHA and PMeOA (with the release of small low-fuel molecules) and the thermal degradation of PBO. The magnatude of the weight loss associated with each step is dependant on the percent of PHA, PMeOA, and aliphatic content in the copolymer.

Introduction

Organic polymers have found widespread use due to their versatility as plastics, rubbers, fibers, adhesives, and coatings. These materials have several advantages over other traditional materials (metals and ceramics): such as, low densities and ease of fabrication. However, some inherent deficiencies, such as low softening temperatures and susceptibility to oxidation and thermal decomposition, have restricted their use.[1]

Fire in an enclosed and inescapable area is a major threat to human life. The interiors of an airplane cabin, a submarine, or even a high-rise office building are a few examples of areas with such limited egress. Due to their light-weight and ease of fabrication, polymers have advantages over conventional materials in these applications, however, they also add greatly to the fire threat due to their potential for rapid combustion and heat release.[2] In the United States, fire causes over 6000 deaths and 10 billion dollars of property damage, annually.[3]

The burning process for polymers occurs in three stages. First, the surface of the bulk polymer is thermally decomposed in a non-oxidative manner. The volatile decomposition products are then swept up into the combustion zone where they mix with atmospheric oxygen. This evolution is what feeds fuel to the flame. The third stage is in the flame itself where high temperature oxidation occurs. The oxidation reactions are very exothermic and cause the release of a great deal of heat. This heat can then cause the non-oxidative thermal decomposition of the surface of the bulk materials, leading back to the first stage in a cyclic

process (as shown in **Figure 1**). Interruption of any of these three stages would cause the extinguishing of the fire.

US Air Force has been researching polybenzoxazole (PBO) as a low density, high modulus, high temperature polymer since the 1970s.[4] PBO has been found to have very good fire-safe properties; however, PBO is very difficult to process in to parts. Our goal is the synthesis of PBO prepolymers with high thermal stabilities, high solubilities in common solvents, softening tempertures that will allow thermal processing, and when exposed to high temperatures release volatile low-fuel molecules and become even more thermally stable by becoming a type of PBO.

Experimental Section

Materials

All reactions and purifications were conducted in an inert atmosphere. Dimethylacetamide (DMAC), isophthaloyl dichloride, glutaryl dichloride, anhydrous pyridine, and 3,3'-dimethoxybenzidine were received from Sigma-Aldrich Chemical Company. Methanol and dimethylsulfoxide (DMSO) were received from VWR. 3,3'-dihydroxybenzidine (98%) was received from TCI America. The dimethylacetamide was dried by distillation over barium oxide. Isophthaloyl dichloride and glutaryl dichloride were purified through distillation. 3,3'-dimethoxybenzidine was purified through high temperature sublimation. 3,3'-dihydroxybenzidine was purified through conversion to the hydrochloric salt and subsequent recrystallization from dilute hydrochloric acid. All other reagents were used as received.
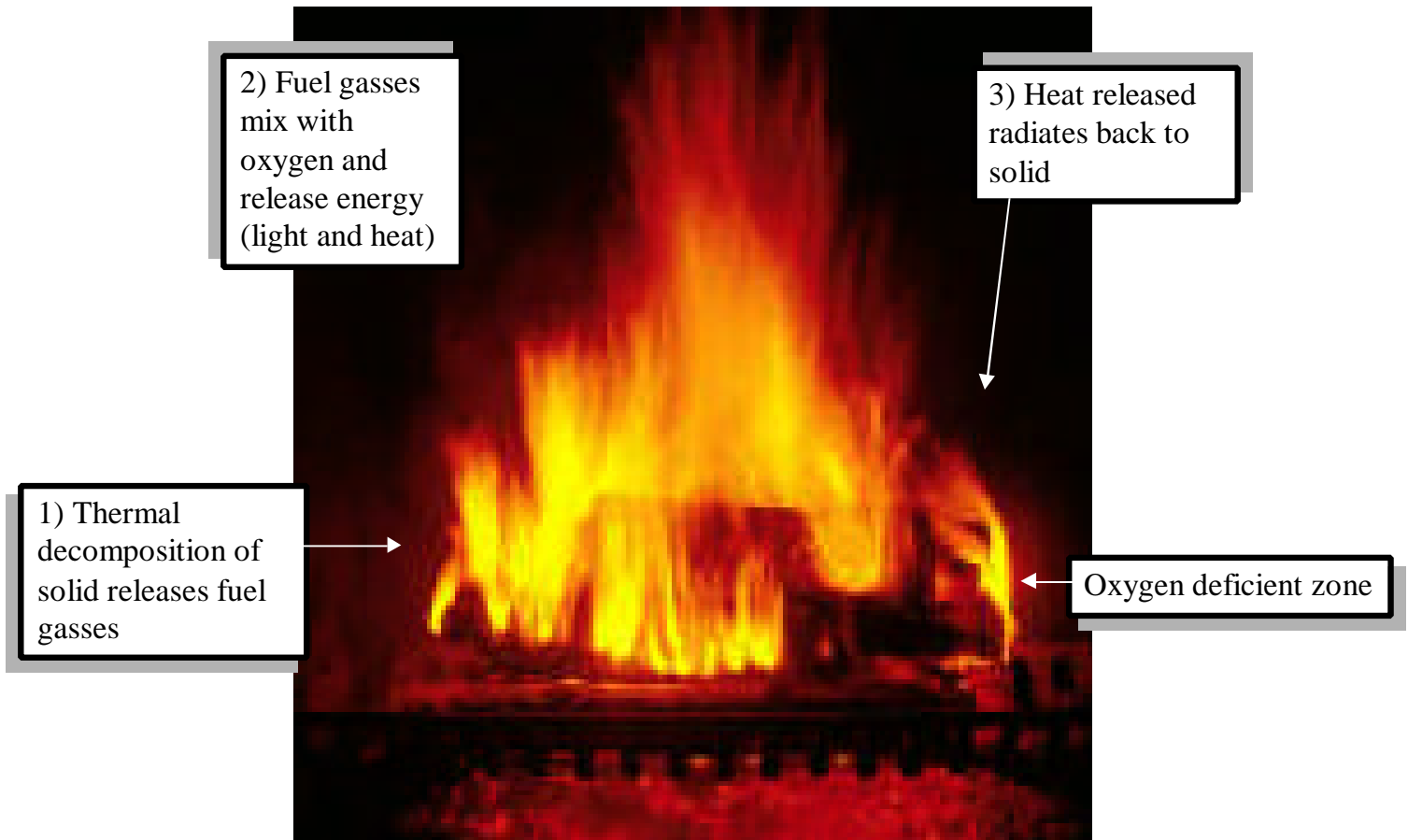
The Fire Cycle

2) Fuel gasses mix with oxygen and release energy (light and heat)

3) Heat released radiates back to solid

1) Thermal decomposition of solid releases fuel gasses

Oxygen deficient zone

Figure 1: The Cycle of Polymer Combustion

General Procedures

Methods. ^{1}H NMR spectra were recorded on a Bruker-Spectrospin DSX 300 MHz NMR using DMSO-d_6 as the solvent.   The University of Massachusetts Graduate School Microanalytical Laboratory performed elemental analysis. Differential scanning calorimetry (DSC) traces were recorded from a DuPont Instruments DSC 2910 Differential Scanning Calorimeter. Thermal gravimetric analysis (TGA) data were obtained on a TA Instruments TGA 2050 Thermogravimetric Analyzer. Thermal mechanical analysis data were produced from a DuPont Instruments TMA 2940 Thermomechanical Analyzer. Microcalorimetry experiments were performed on a FAA Pyrolysis Flow Microcalorimeter.

Synthesis

All of the copolymers were synthesized in a similar manner. The nomenclature used for the polymers consists of four numbers. The first two represent the relative percentages of 3,3'dihydroxybenzidine and 3,3'-dimethoxybenzidine.   The thrid and fourth numbers represent the relative percentages of isophthaloyl dichlorde and glutaryl dichlorde respectively. The copolymers were prepared with stoichiometricly equivalent amounts of amino functional groups and acid chloride functional groups. The copolymerization of the 100% dimethoxybenzidine with 100% isophthaloyl dichloride monomers will be illustrated as an example for these materials.

0/100/100/0 (PMeOA). In a nitrogen atmosphere dry-box, 3,3'-dimethoxybenzidine (12.43g, 50.9mmol) was added to a 500ml three neck round bottom flask equipped with a flow control adapter with stopcock in one of the side necks. The 3,3'-dimethoxybenzidine was slurried in dry DMAC (90ml) with anhydrous pyridine (11ml, 0.136mol). Isophthaloyl dichloride (10.33g, 50.9mmol) was dissolved in a dropping funnel with DMAC (30ml). The flask and dropping funnel were then stoppered and brought from the dry-box to a nitrogen/vacuum manifold. While maintaining the nitrogen atmosphere, the dropping funnel was attached to the other side neck of the round bottom flask. A glass shaft mechanical stirrer was added through the middle neck of the flask. The flask was then cooled in an ice bath. After 30 minutes, the isophthaloyl solution was slowly added drop-wise with vigorous stirring, while still maintaining the ice bath. The ice bath was maintained for another hour, after which the ice was allowed to melt, and the viscous yellow solution slowly warmed to room temperature. After 20 hours of stirring, the yellow solution was slowly poured into 1500ml of rapidly stirring methanol. The resulting light yellow fibers were then filtered and added to a blender with distilled water. The chopped polymer was then filtered and washed with distilled water until the filtrate was of the same pH as the distilled water. The polymer was then washed with acetone and dried in a vacuum oven at 160°C for 24hrs, yielding 18.01g of light yellow polymer (94.5% yield).

Results and Discussion

The general synthetic scheme for the poly(hydroxy amide) family of fire-safe "smart" copolymers is given in **Figure 2**. This family of polymers has been seen to yield polybenzoxazole (PBO) when heated to their cyclization temperature (Figure 2). The low

temperature synthesis allows the formation of the "smart" polymer without inducing extensive PBO ring closure. The chemical structure of the PMeOA was confirmed from ^{1}H (**Figure 3**) and ^{13}C NMR as well as by elemental analysis. ^{1}H NMR examples of a few members of these copolymers is shown in **Figure 4**. These polymers are soluble in DMAC, DMSO, and NMP.

Thermal analysis of these copolymers can be used to help determine both their fire-safe properties and their processability. TGA, DSC, and TMA were all performed with heating rates of 10°C/min in a nitrogen atmosphere. Thermogravimetric analysis (TGA) for these polymers shows up to three distinct degradation steps (**Figure 5**). The first step, occuring at ~250°C, arises from the cyclization of the repeat units involving the 3,3-dihydroxybenzidine to PBO. The second step beginning at ~350°C indicated the cyclization of the 3,3'-dimethoxybenzidine repeat units to PBO. Some chain degradation also occurs at this temperature. The third step at ~600°C is indicative of PBO becoming carbonic char. Typical char yields are in the range of 40-50%. However, the copolymer with 100% glutaryl dichloride yields only ~20% char at 900°C. This shows the weakening of the polymer main chain with extensive addition of aliphatic linkages. DSC analysis shows that copolymers with higher percentages of 3,3'-dihydroxybenzidine do not exhibit a glass transition temperature (**Figure 6**) while those with 25% do. The Tg
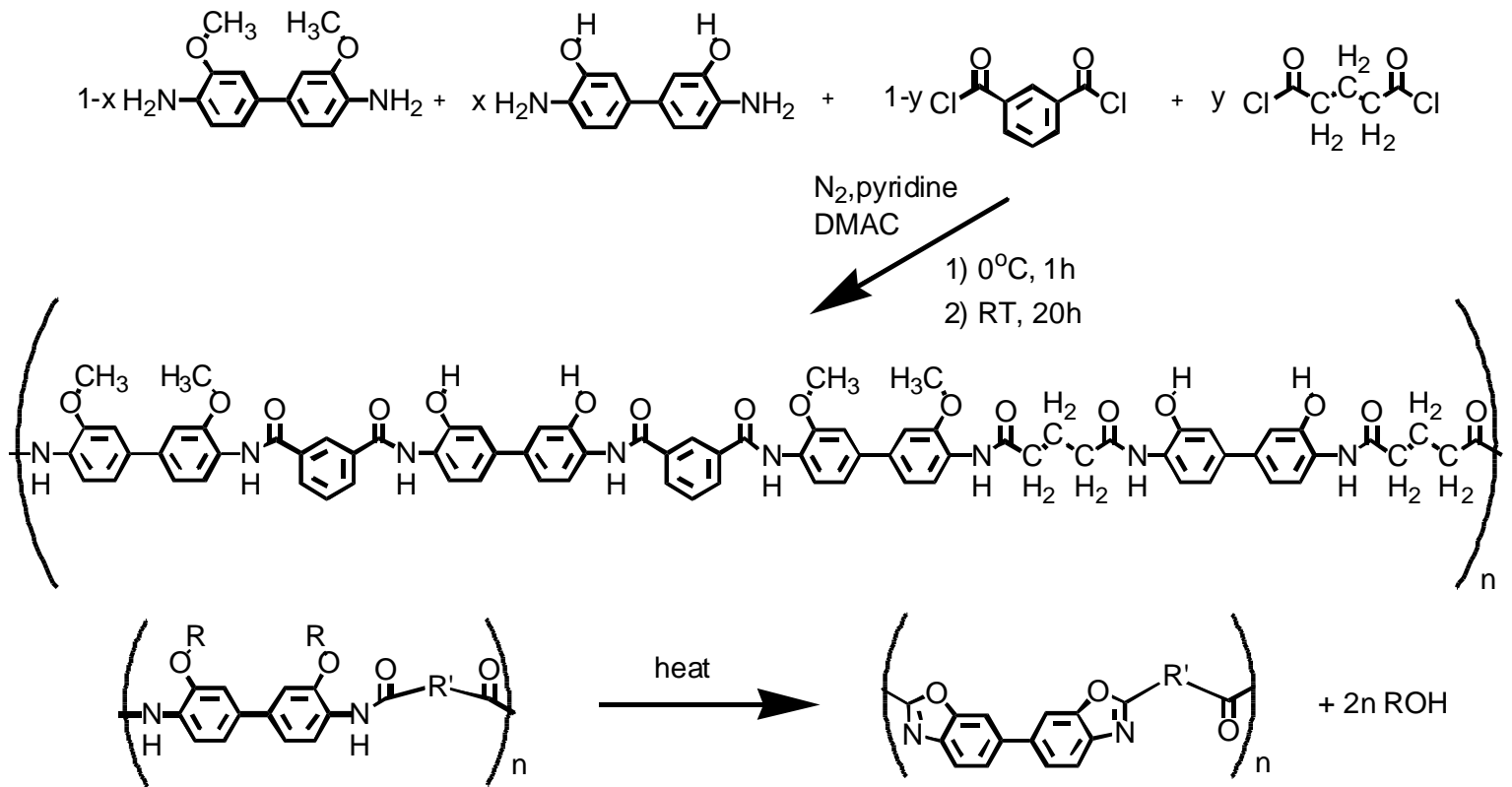
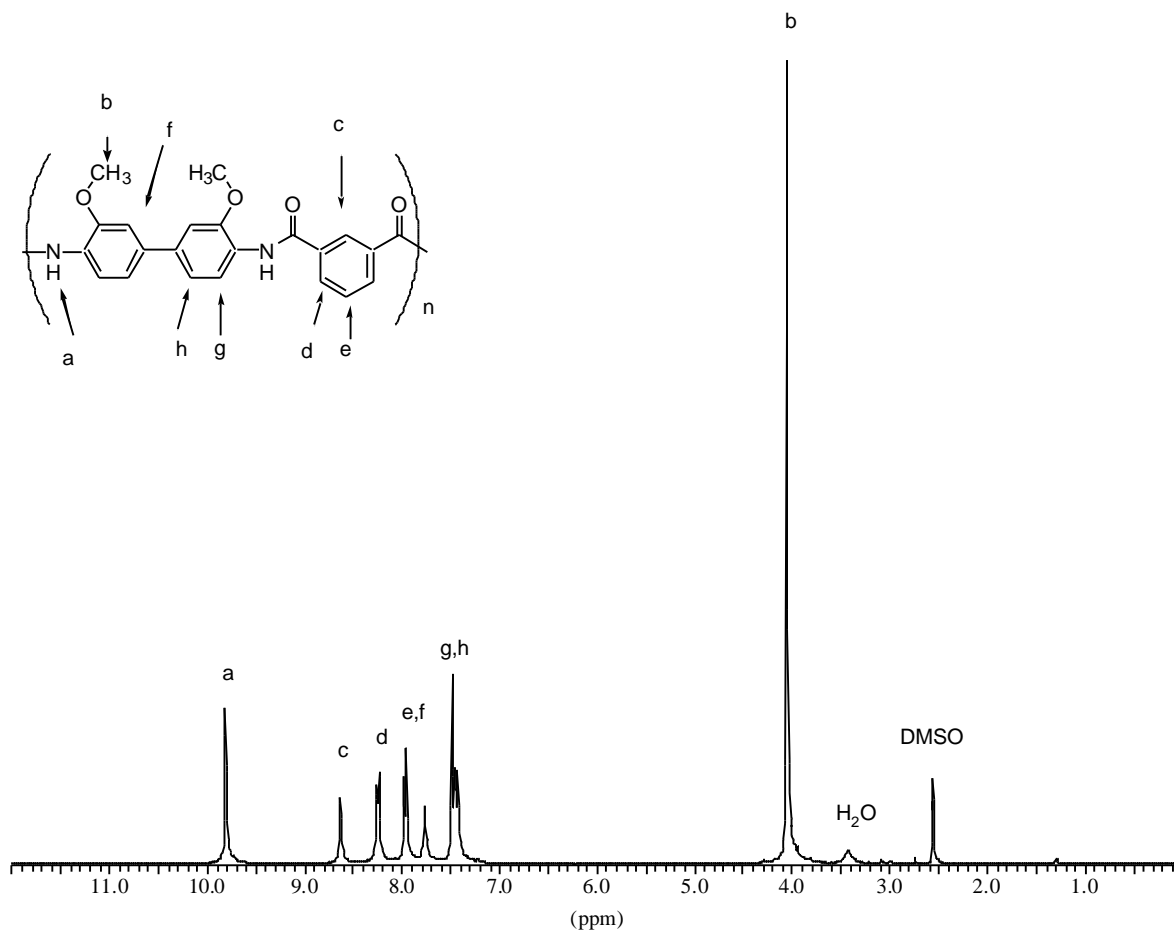**Figure 2**: Synthetic Scheme of PHA/PMeOA "Smart" Copolymers
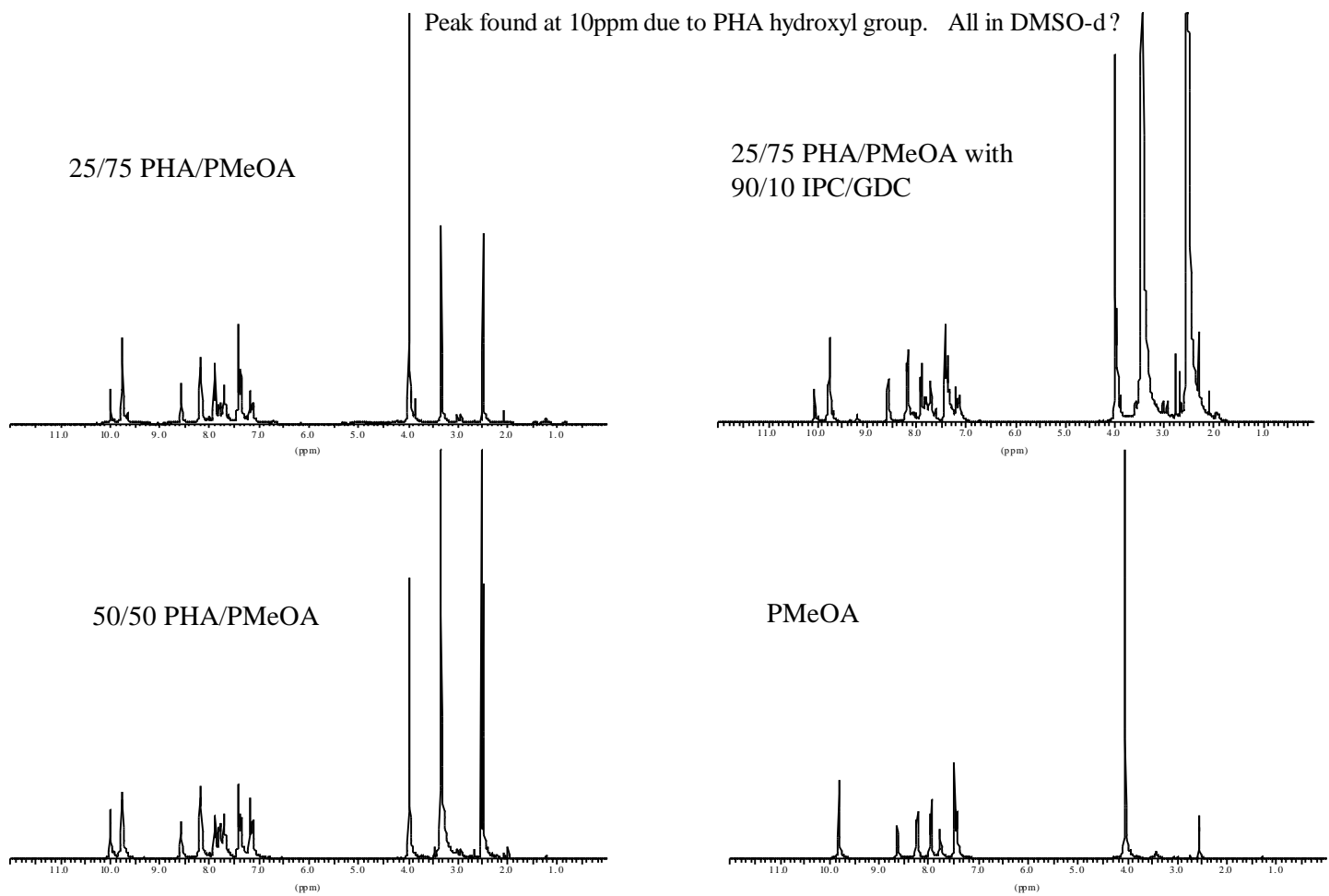
Figure 3: Proton NMR of 0/100/100/0

Peak found at 10ppm due to PHA hydroxyl group.   All in DMSO-d ?

25/75 PHA/PMeOA

25/75 PHA/PMeOA with
90/10 IPC/GDC

50/50 PHA/PMeOA

PMeOA

Figure 4: Proton NMR of a Few Copolymers
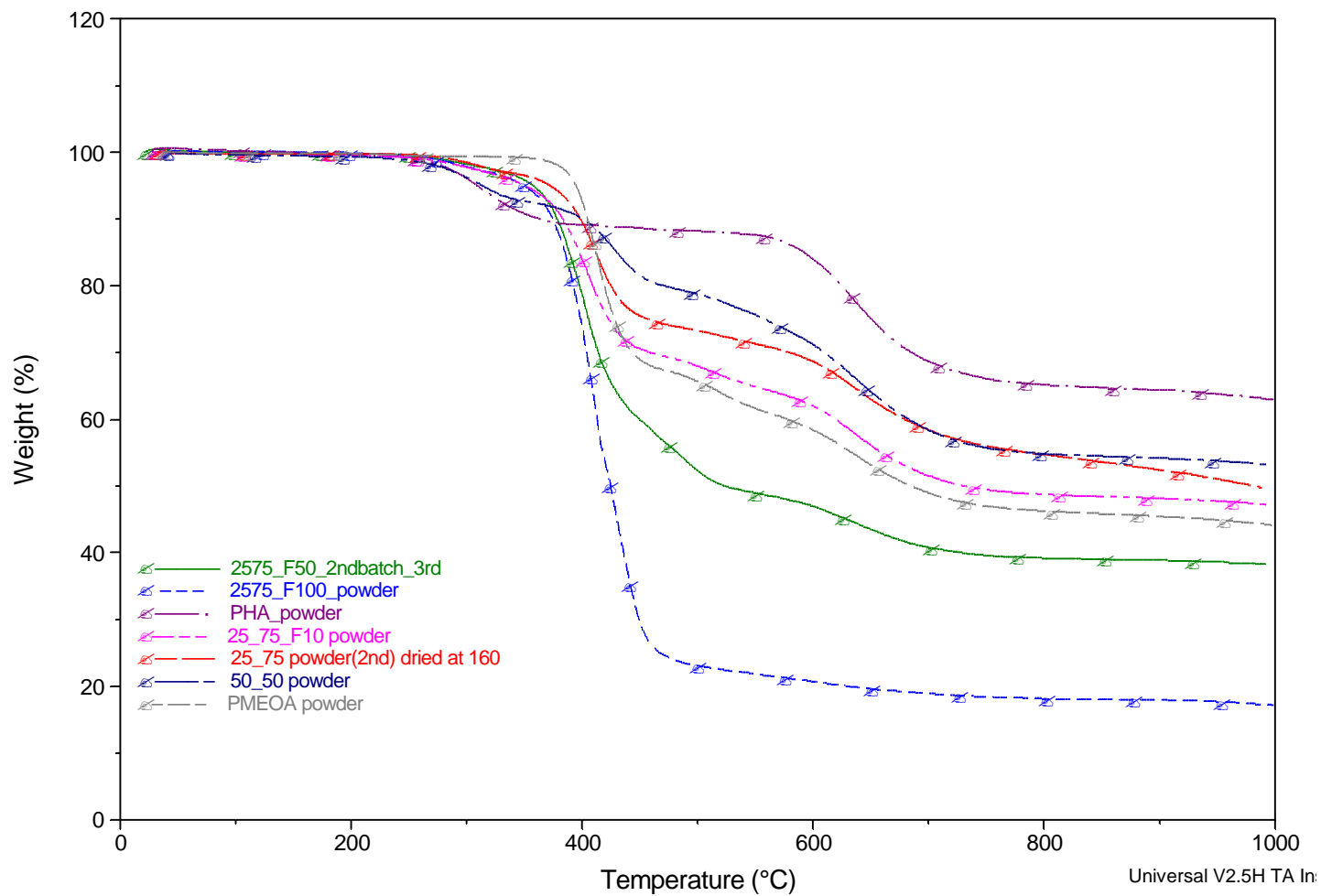
Figure 5: TGA Analysis of the PHA/PMeOA Copolymers

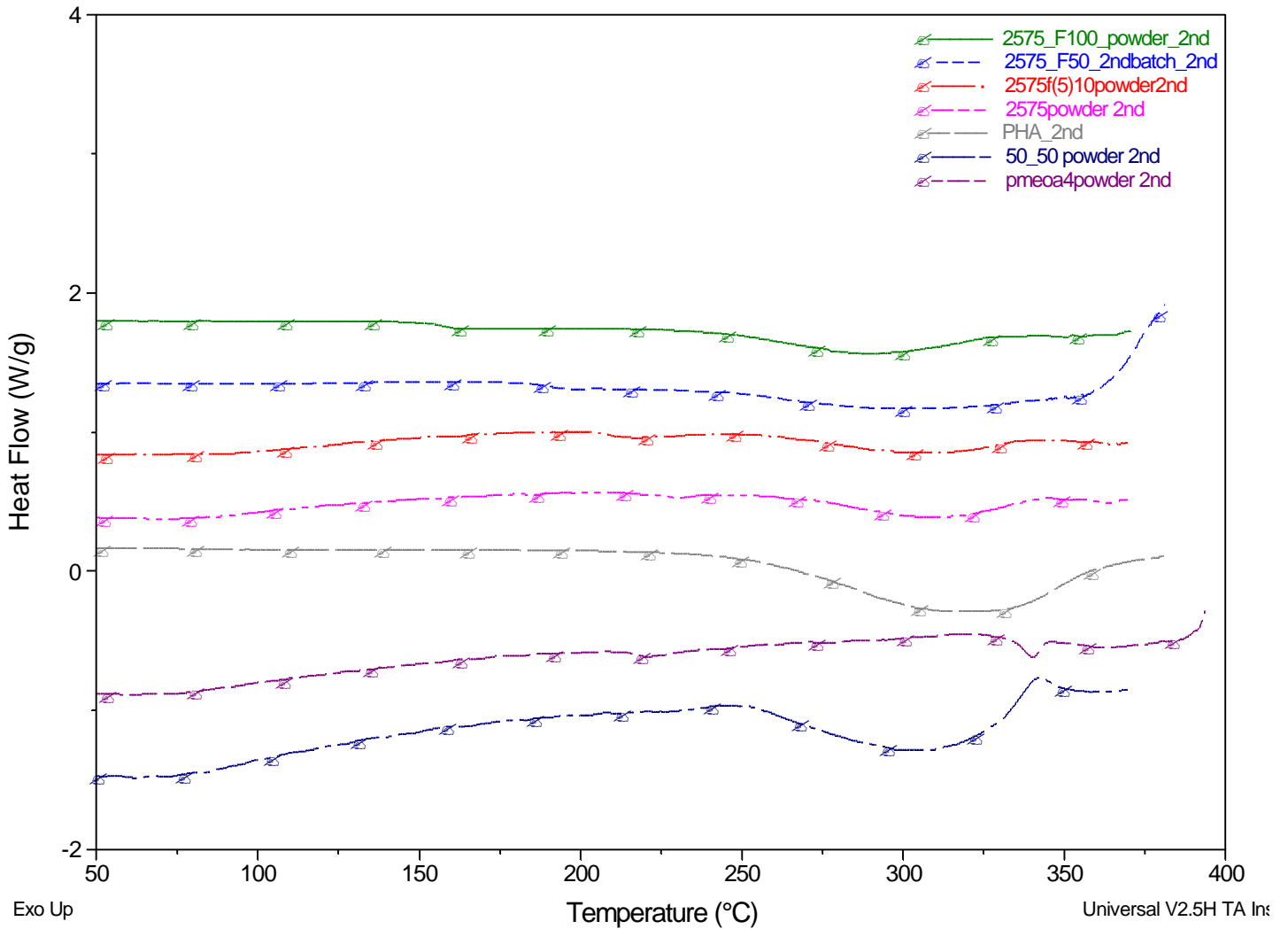| Polymer	Tg
25 / 75 / 0 / 100 P HA / P Me O A / I P C / GD C	150 . 9
25 / 75 / 50 / 50 P HA / P Me O A / I P C / GD C	190 . 0
25 / 75 / 90 / 10 P HA / P Me O A / I P C / GD C	207 . 2
25 / 75 P HA / P Me O A	226 . 1
50 / 50 P HA / P Me O A	N / A
P HA	N / A
P Me O A	218 . 2

Figure 6: DSC Scans of PHA/PMeoA Copolymers

can also be lowered by incorporation of the flexible glutaryl dichloride. While the addition

of flexible linkages lowers both the Tgs of the polymer and the first stage cyclization, the rate

of temperature decline is greater for the change in Tg. This means that the processing

window can be expanded through flexible group addition. The 0/100/100/0 (fully aromatic)

polymer shows both a Tg and a melting endotherm The crystalline melting endotherm is not

present in the DSC scan of any of the other polymers. This is most likely due to a disruption

of the crystals from both the randomization of the chain's cross-sectional area, thus

disrupting the chain packing, and the additional influence of the hydrogen bonding from the

3,3'dihydroxybenzidine units. Pyrolysis flow microcalorimetry analysis of these and some

other common polymers has been conducted. The microcalorimetry results were collected as

follows: a sample (1mg ± .1mg) is weighted into an alumna boat. The sample is then loaded

into the tip of a pyroprobe and ramped to 1200°C at 5°C/s in a nitrogen atmosphere. The

volatiles are swept through a heated (225°C) interface into an oven with a nitrogen/oxygen

flow. The heat released from the combustion of the gasses is measured and reported as the

heat release capacity (the peak heat released during combustion) and the total heat released.

These values combined with the char yield are related to two of the stages of combustion

mentioned above. The char yield is directly related to the amount of fuel evolved from the

sample. The heat release capacity and the total heat released are related to the amount of heat

generated to the catalytic cycle of polymer combustion (stage 3 above). Therefore fire-safe

polymers should have low heat release capacity, low total heat release, and high char yields.

Table 1 displays these results. As can be seen from the table, most of the polymers from the

PHA family have lower heat release capacities and total heat releases than the commodity

polymers tested. The addition of the flexible glutaryl dichloride to the copolymer shows a

Polymer	Heat Release Capacity (J/g ·K)	Total Heat Release (kJ/g)
PE	1558	40.4
PC	382	19.3
Kevlar	292	15.2
PHA	42	10
25/75/100/0 PHA/PMeOA/IPC/GDC	50	11
25/75/90/10 PHA/PMeOA/IPC/GDC	66	12
25/75/50/50 PHA/PMeOA/IPC/GDC	224	16.3
25/75/0/100 PHA/PMeOA	450	20.4
50/50 PHA/PMeOA	33	11
PMeOA	130	17

Table 1: Microcalorimetry Results

strong influence on these heat release characteristics. Addition of both types of benzidines to the copolymer shows a lowering of the heat release capacity by spreading the heat release to a larger temperature range.

While the many of the PHA/PMeOA copolymers display Tg's, the processing window between the Tg and the onset for the first stage of cyclization is limited to about 50°C (except for the fully flexible polymer which has a window of ~100°C). Therefore films were cast and tested using TMA. These free standing films were found to contain ~10% solvent (DMSO). The films were tested with a constant force of 0.1N. **Figure 7** illustrates the results. As can be seen, the order of the relative softening temperatures for these polymers corresponds well with the order seen from the Tgs. However, the softening temperatures have been lowered by as much as 40°C. The residual solvent acts as a plastisizer for these materials. This depression of the softening temperatures allows an expanding of the thermal-processing window, as long as the material is processed before extensive solvent loss.

Conclusions

The "smart" polymeric materials derived from 3,3'-dyhydroxybenzidine, 3,3'-dimethoxybenzidine, isophthalyol dichloride, and glutaryl dichloride hav been synthesized and characterized. The synthesis occurs in solution at low temperature, preventing premature ring cyclization to PBO. The polymer structures were confirmed from ^{1}H-, ^{13}C-NMR, and elemental analysis. TGA displays up to three-step degradations for these copolymers. The first step is associated with ring closure of the 3,3'-dihydroxybenzidine repeat units to PBO, at ~250°C, the second step is associated with ring closure of the 3,3'-dimethoxybenzidine
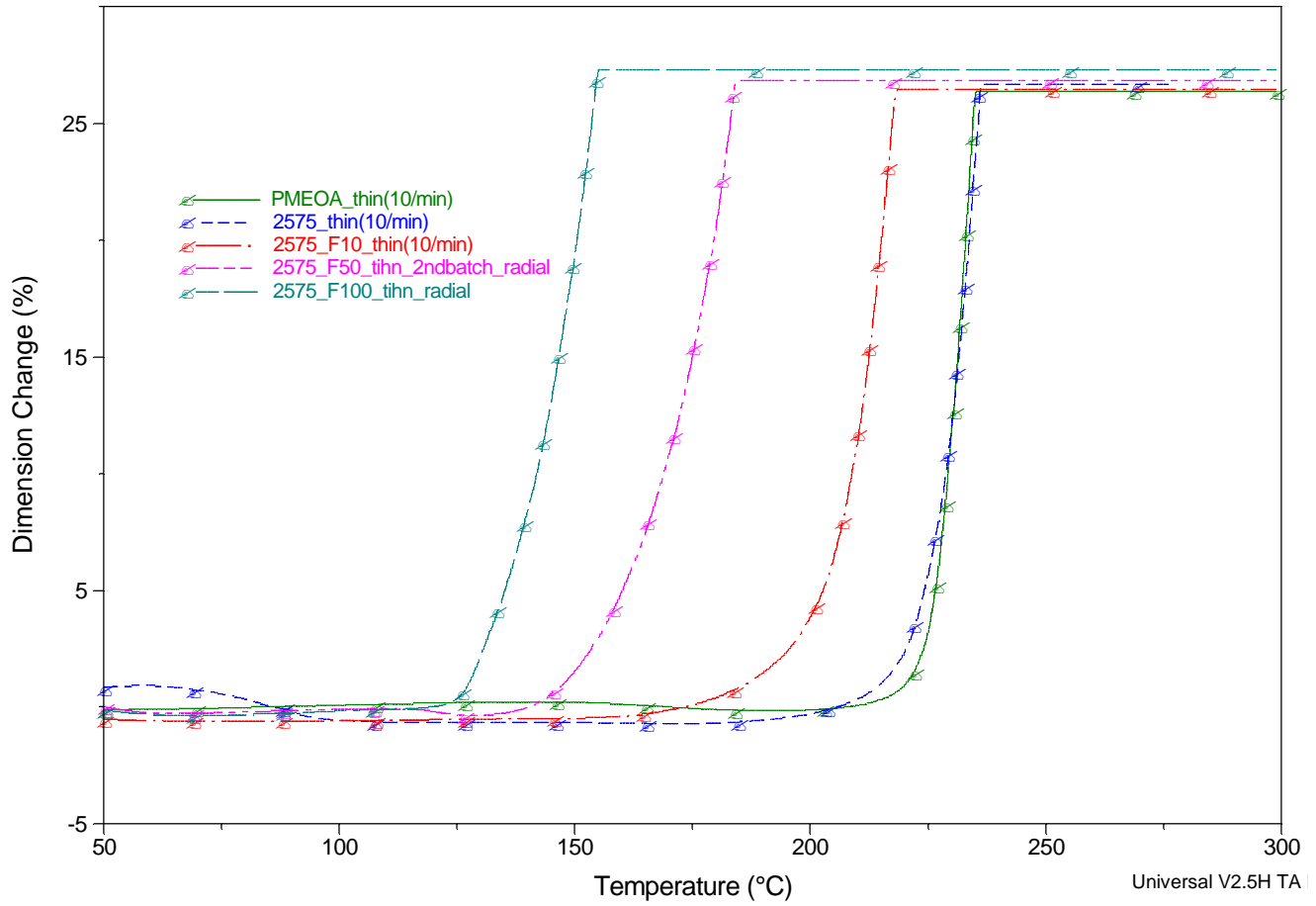
Figure 7: TMA of PHA/PMeOA Copolymers

repeat units to PBO (plus a little main chain degradation), at ~350ºC, and the third is the degradation of PBO, at 600ºC. DSC and TMA have shown Tgs and softening temperatures as low as 125°C for this family of polymers, thus allowing thermal processing prior to ring closure. Microcalorimetry has shown that these polymers have tunable heat release capacity, total heat release, and high char yields by varying the percentage of flexible linkages in the polymer main chain.

([1]) Alger, M.S.M in *Specialty Polymers* editor Dyson, R.W., Blackie Academic & Professional, London, UK, 1998, p37.

([2]) For more information see: www.pse.umass.edu/cumirp/clusterf.html

([3]) Nelson, G. L. Fire and Polymers II: Materials and Tests for Hazard Prevention; Nelson, G. L., Ed.; American Chemical Society: Washington, D.C., 1999; Vol. 599, p. 1.

([4]) So, Y.-H. *Prog Polym Sci*, **2000**, *25(1)*, 137.