UNIVERSITY OF MASSACHUSETTS AMHERST

Center for UMass Industry Research on Polymers (CUMIRP)

Research Cluster F

Fire-Safe Polymers and Polymer Composites

FINAL REPORT
MARCH 24, 2000

Richard Farris, Principal Investigator

Federal Aviation Administration

Grant # 95-G-015

Summary of Completed Project: High Performance Fire – Safe Polymeric Materials (CUMIRP Cluster F)

The CUMIRP Cluster "F" Program entitled, "Fire-Safe Polymers and Polymer Composites", was a $1,400,000 four-year research program that was initiated with the FAA in 1995. The goal was to develop polymers and polymeric composites that had an order of magnitude improvement in fire-safety characteristics when compared to those materials that are allowed to be used in today's commercial aircraft interiors. In an effort to efficiently and effectively commercialize promising research results, industrial companies were encouraged to join the program.

The research involved seven faculty specializing in three distinct areas: 1) synthesis of new flame-resistant polymers, 2) physical and mechanical characterization including flame calorimetry, and 3) molecular modeling. Several deliberate approaches were taken to design fire-resistant polymeric materials including materials with high decomposition temperatures, high char yields, built in heat sinks, and the generation of flame suppressing components from the molecular backbone of the polymer when the material is subjected to very high heats. The most significant developments were: the two material families based on Poly(hydroxyamides), (PHA's), and derivatives based on chloral bisphenol, (BPC's), and the development of measures of flammability requiring very small amounts of material.

The PHA's are precursors to Polybenzoxazole's (PBO) one of the most flame resistant polymers known. Unlike the PBO based materials, which are only soluble in very strong acids, PHA's are soluble in typical solvents and can be used in fibers and coating applications using friendlier processing methods. They have excellent mechanical properties similar to polyimide materials. Upon exposure to high heat, these materials cyclize to become PBO's and in doing so, liberate water or other products of cyclization which have been designed to suppress fire. Also, the cyclization process acts as a heat sink. These materials have attracted considerable interest by our sponsors and outside organizations. PHA's are among the best ever tested by the FAA in terms of their fire-resistance.

The polymers based on BPC have been the focus of considerable UMass research. This simple substitution in polycarbonate or other polyester materials has a very dramatic effect. It greatly increases the char yield and reduces the maximum rate of heat production during a fire by about a factor of 20. Both thermosetting and thermoplastic materials can be made utilizing this family of materials. This type of chemistry was studied many years ago by a Polish group and by General Electric, but was never commercialized. We have reevaluated many of these materials as well as designed new materials based on this type of chemistry. Polyesters made at UMass rank as the best material tested at the FAA for flame resistance.

Another significant development is that UMass now has three methods of evaluating flammability that are consistent with the FAA requirements and these methods

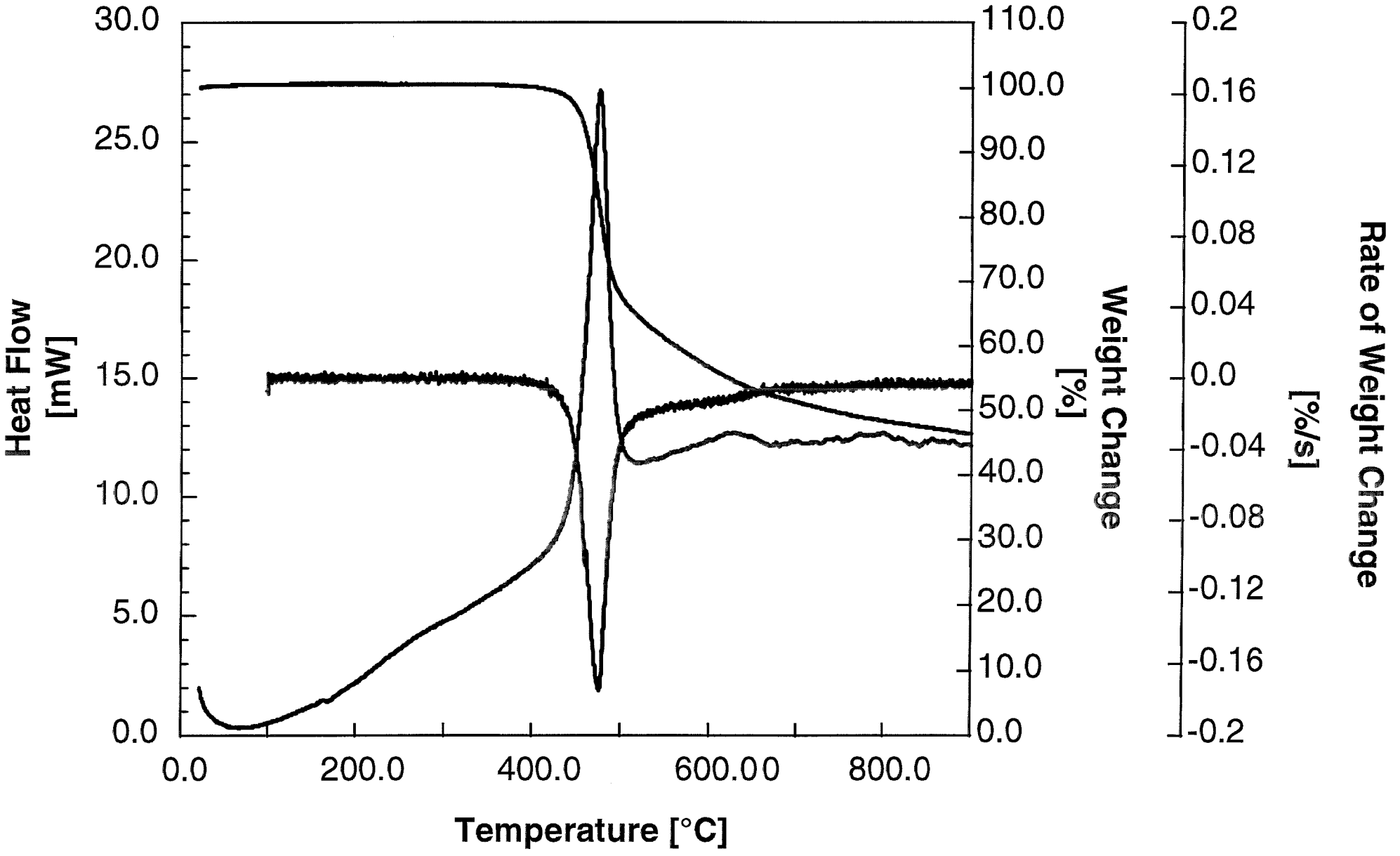
only require milligrams of material. One method is based on the FAA Micro-flame calorimeter, which we have replicated in our laboratories, and is based on oxygen consumption. The other is a pyrolosis GC/MS method that identifies the products and amounts of decomposition species so that the heats of combustion can be calculated. The last method involves using a simultaneous DSC/TGA combined with GC/MS to study the thermodynamics of decomposition as well as the products generated. These methods greatly assist the development of new materials since they can be assessed for their flammability characteristics very early in the synthetic process.

Decomposition Behavior of Bisphenol-C-Based Materials

Jennifer R. Stewart, Richard J. Farris and
Bruce M. Novak

October 20, 1999

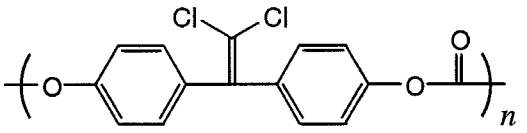
Simultaneous TGA/DSC Data for BPC-Polycarbonate



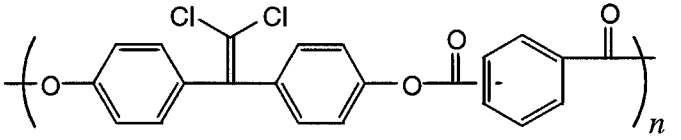
TGA/DSC Data For Bisphenol-C-Based Materials

	Heat of Decomposition (J/g) (kJ/mole)	Temperature at Maximum of Exotherm (°C)	Char Yield at 700°C (%)	Temperature at Maximum Rate of Mass Loss (°C)
BPC-PC	+204 (62.6)	472	51	472
BPC-PA	+115 (47.3)	466	52	472
BPC-S8-PE	+148 (66.1)	348	40	351
BPC-S2-PE	+125 (45.4)	416	40	411
BPC-Br-PA	+97 (55.4)	456	39	457
BPC	+143 (40.1)	265	46	263
DPE-BPC	+91 (44.5)	445	25	420

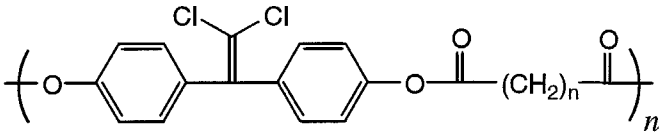
Bisphenol C Based Materials



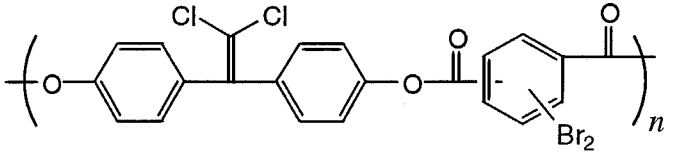
BPC-PC



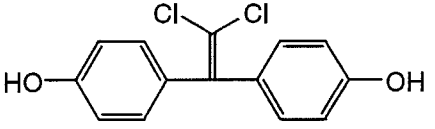
BPC-PA



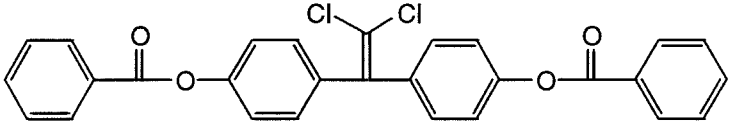
n = 2 BPC-S2-PE
n = 8 BPC-S8-PE



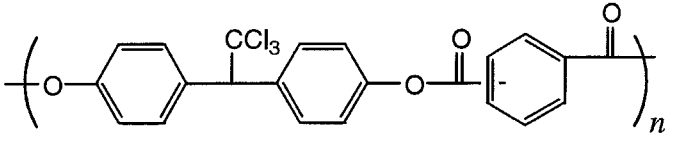
BPC-Br-PA



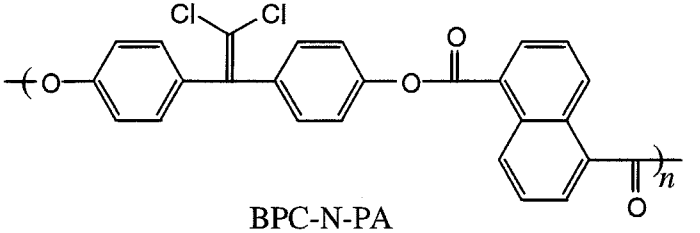
BPC



DPE-BPC

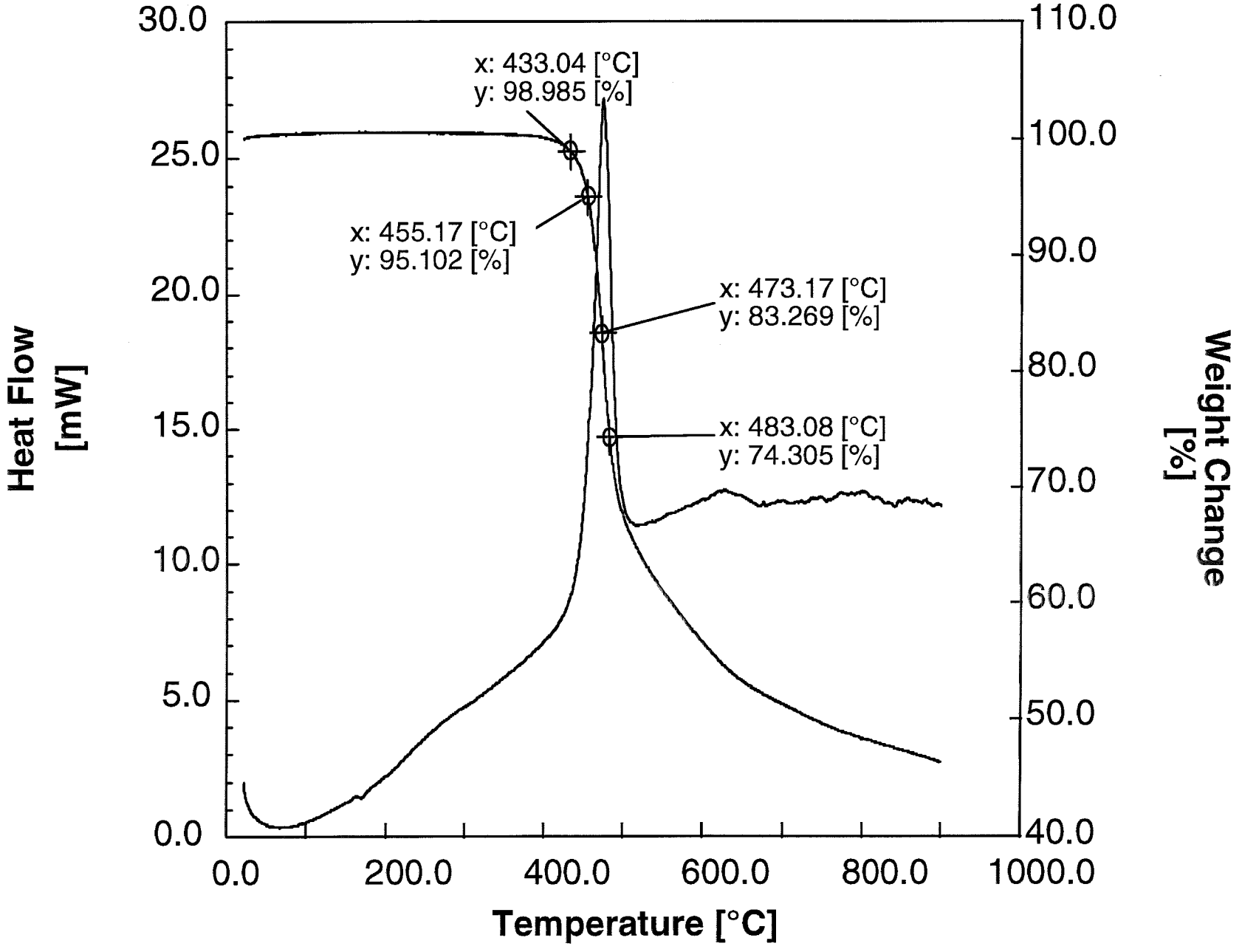


T-PA

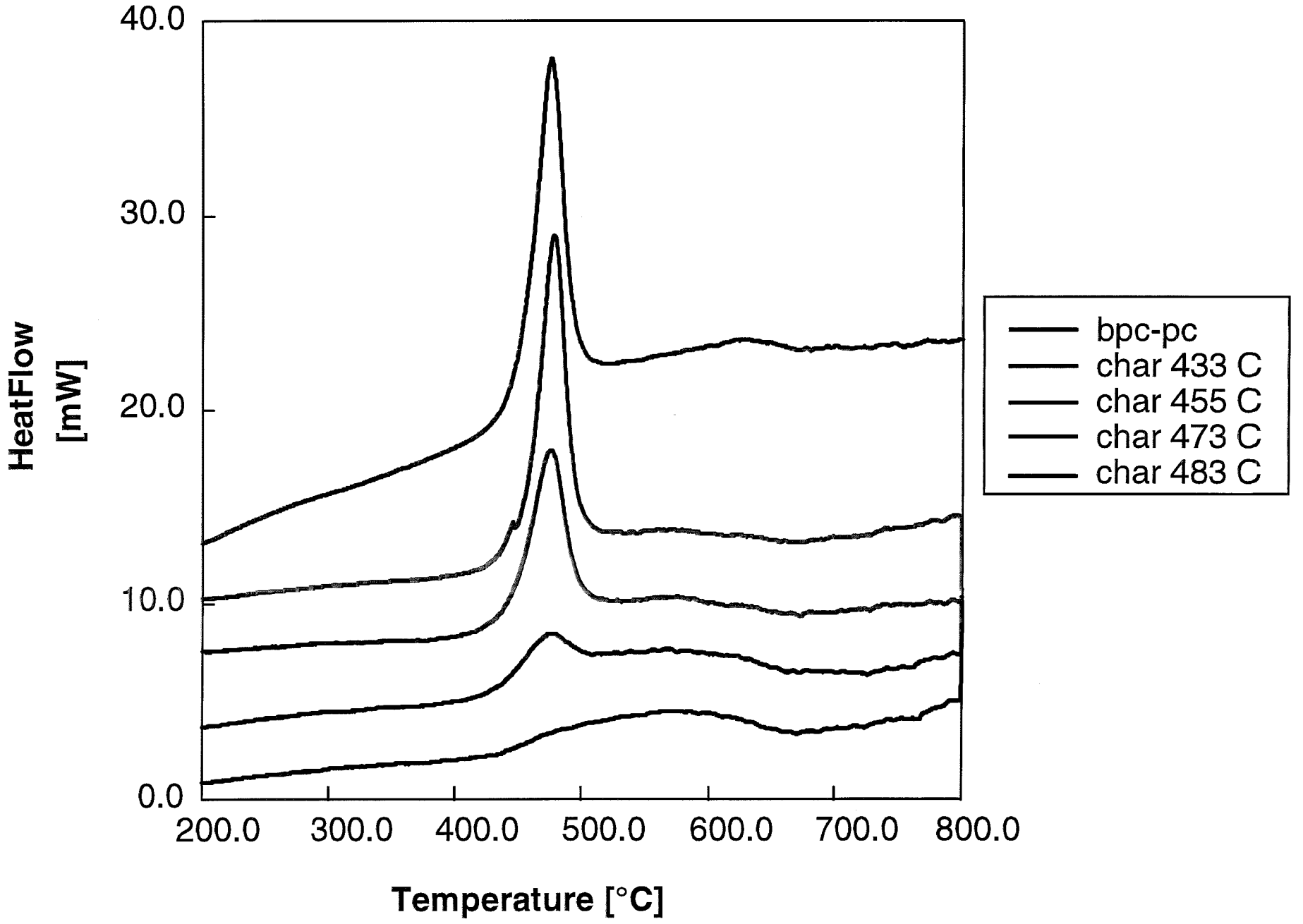


BPC-N-PA

Samples For Study of Decomposition



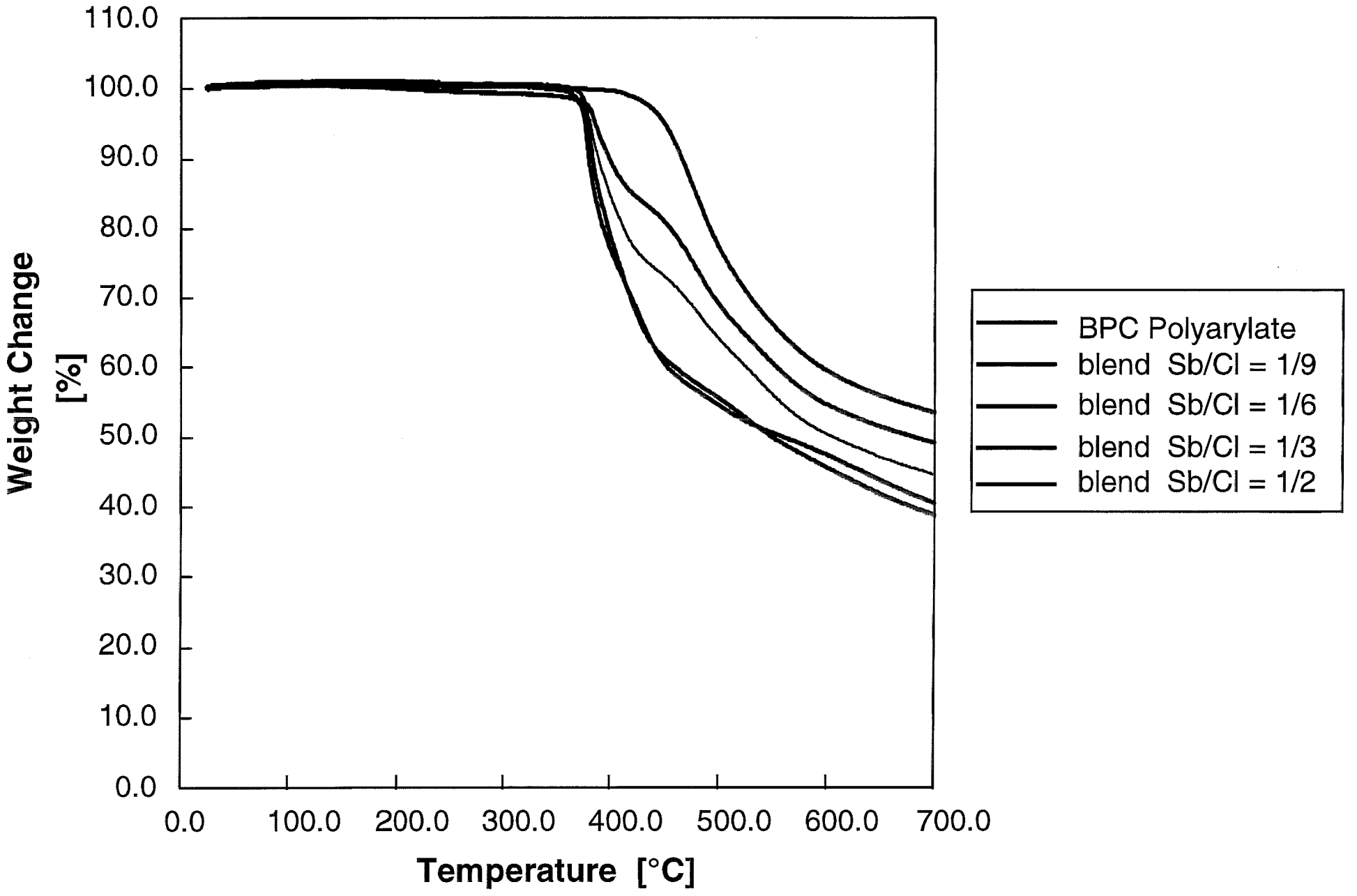
Residual Heat of Decomposition



Summary of TGA/DSC Data

	Heat of Decomposition (J/g)	Peak of Exotherm (°C)	Peak of Mass Loss Rate (°C)
Control	394	476	475
433°C	319	478	475
455°C	294	475	474
473°C	206	475	475
483°C	128	--	530

Effect of Sb_2O_3 on the Decomposition of BPC-Polyarylate



Possible Mechanisms

$$Sb_2O_3 + 6\,HCl \xrightarrow{\Delta} 2\,SbCl_3 + 3\,H_2O$$

$$Sb_2O_3 + 2\,HCl \xrightarrow{\Delta} 2\,SbOCl + H_2O$$

$$5\,SbOCl\,(s) \xrightarrow{245\text{-}280\ C} Sb_4O_5Cl_2\,(s) + SbCl_3$$

$$4\,SbOCl_2\,(s) \xrightarrow{410\text{-}475\ C} Sb_4O_4Cl\,(s) + SbCl_3$$

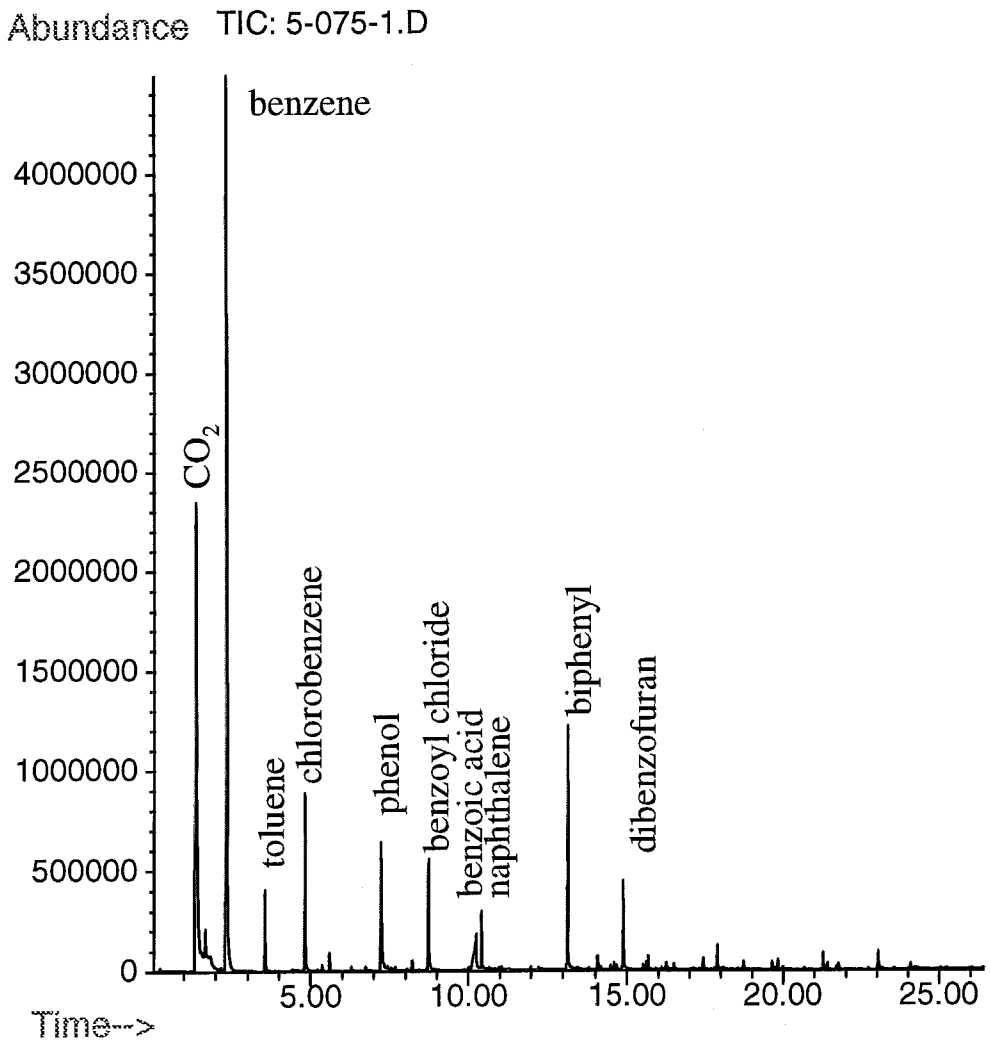
$$3\,SbOCl\,(s) \xrightarrow{475\text{-}565\ C} 4\,Sb_2O_3\,(s) + SbCl_3$$

$$Sb_2O_3\,(s) \xrightarrow{658\ C} Sb_2O_3$$

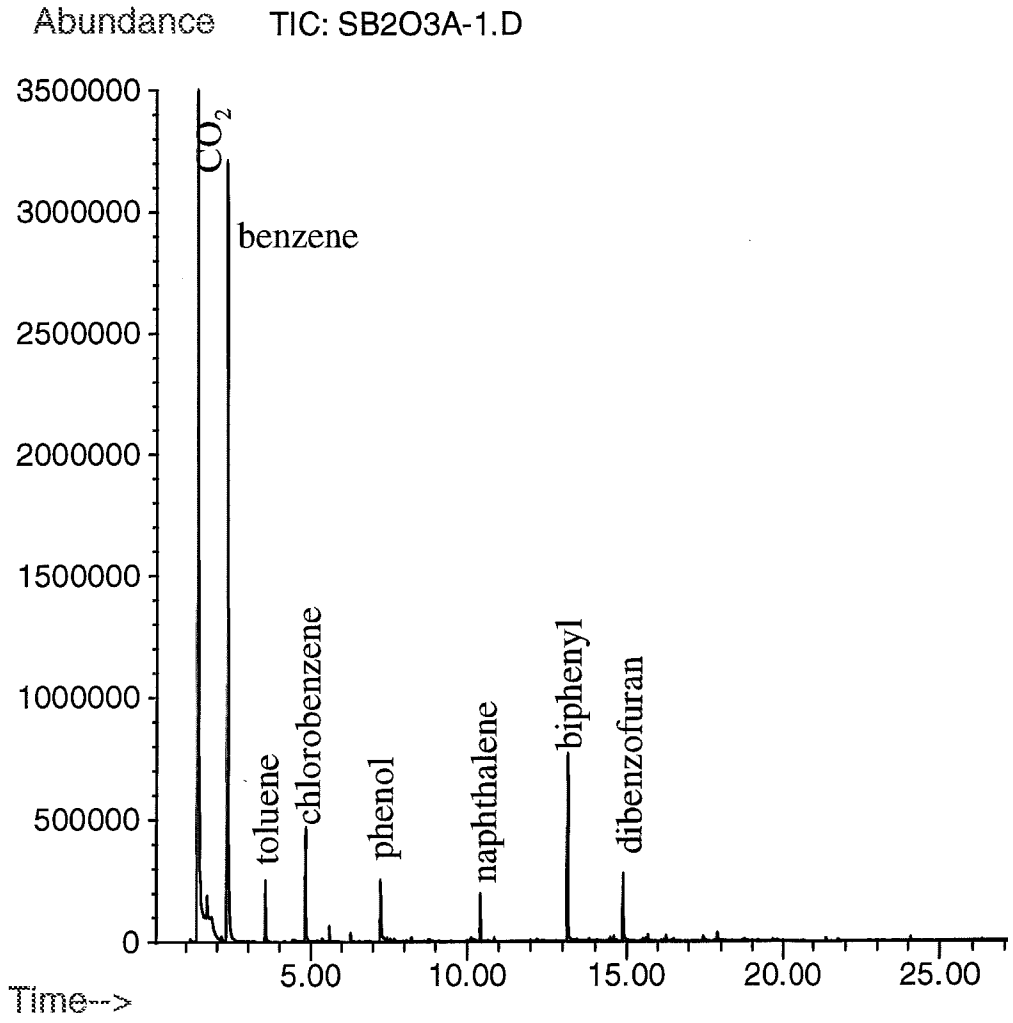
Effect of Antimony Oxide on Decomposition

Weight Percent of Sb_2O_3 (wt %)	Sb/Cl ratio	Char Yield (%)	Char Yield Based on Polymer Mass (%)
0		52	52
7.2	1/9	49	53
10	1/6	45	50
20	1/3	38	55
26	1/2	40	48

Decomposition Products

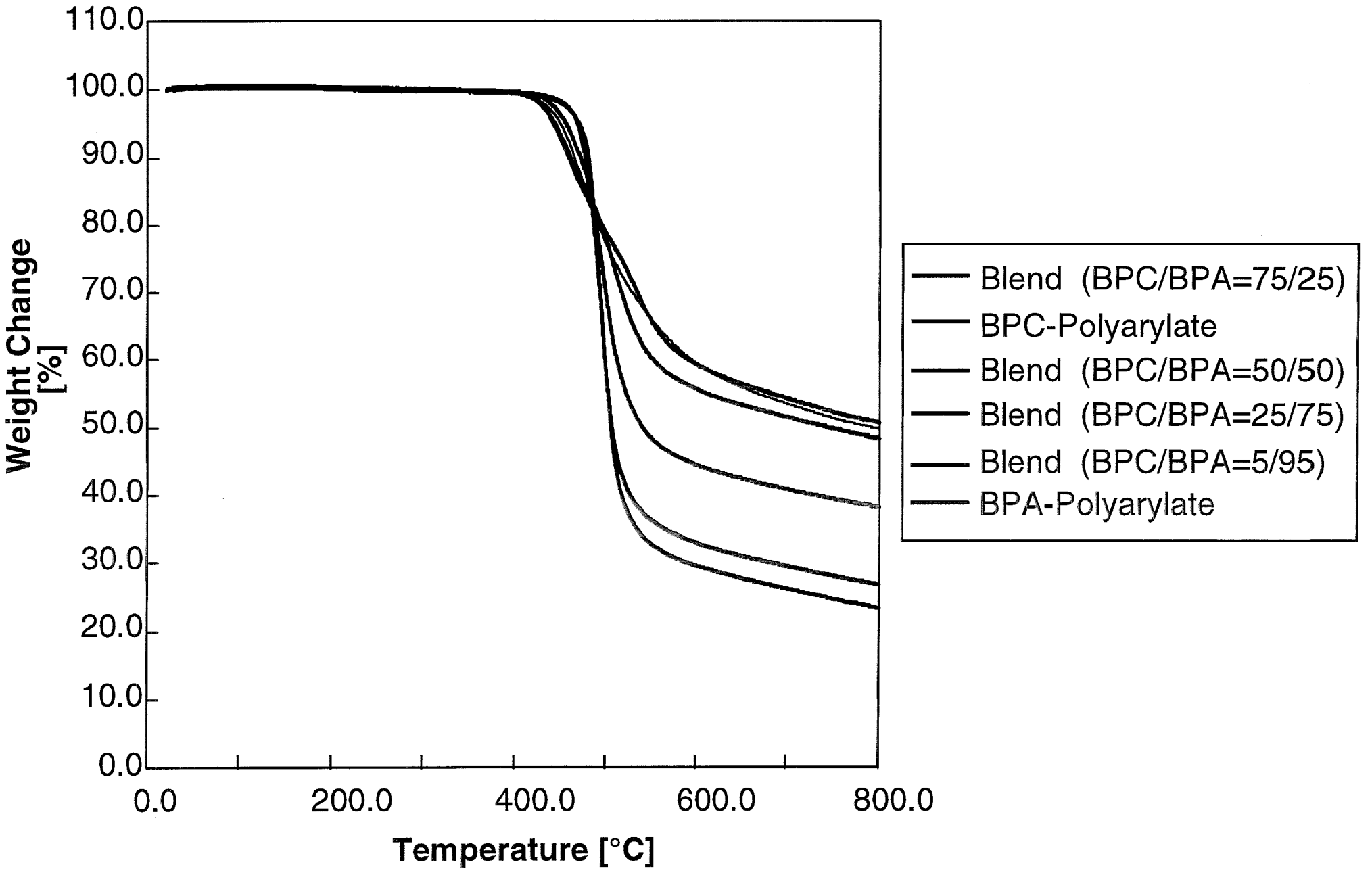


BPC-Polyarylate
1200 C

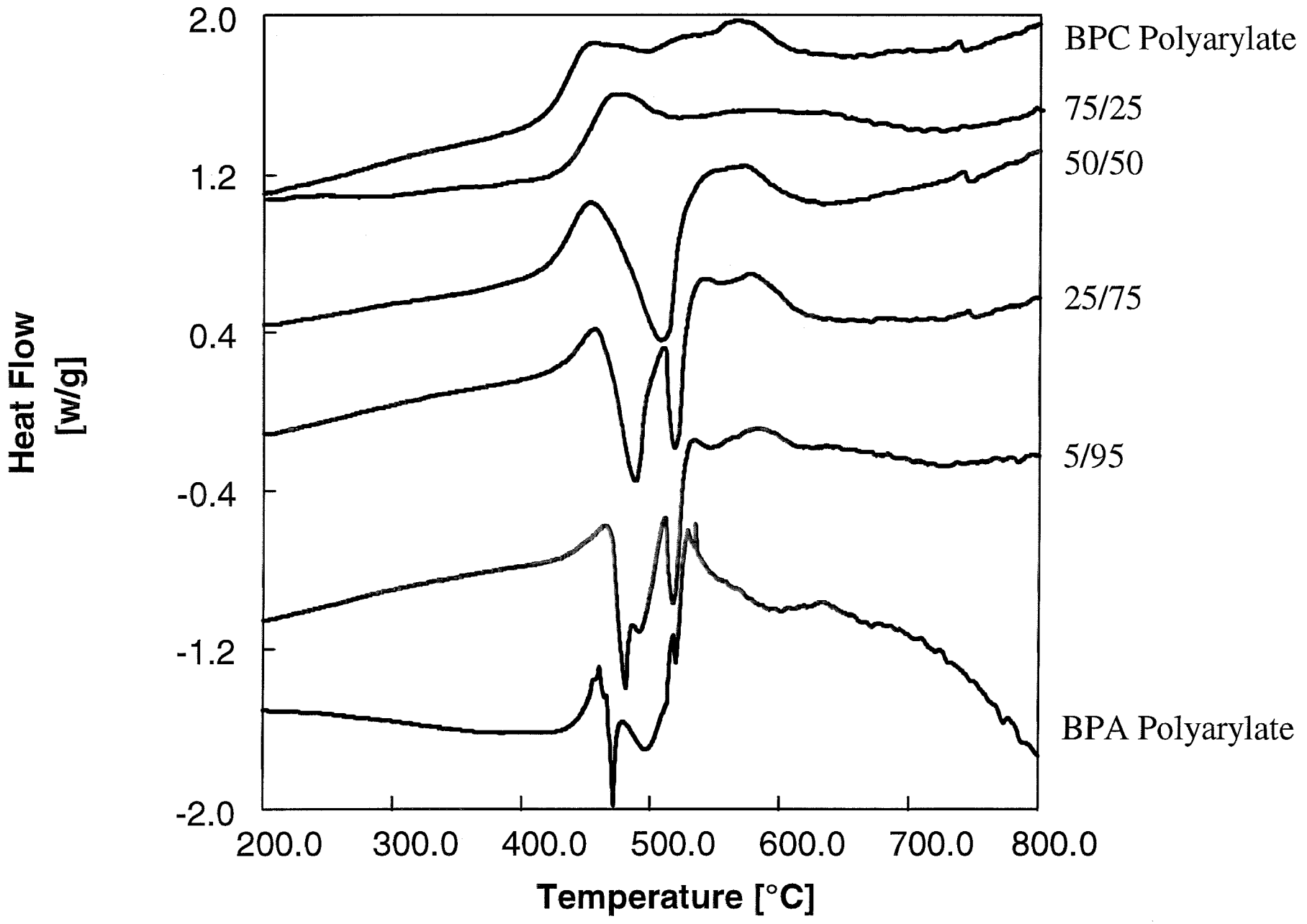


BPC-Polyarylate with 20 wt% Sb_2O_3
1200 C

Polyarylate Blends



Decomposition Behavior of Polyarylate Blends



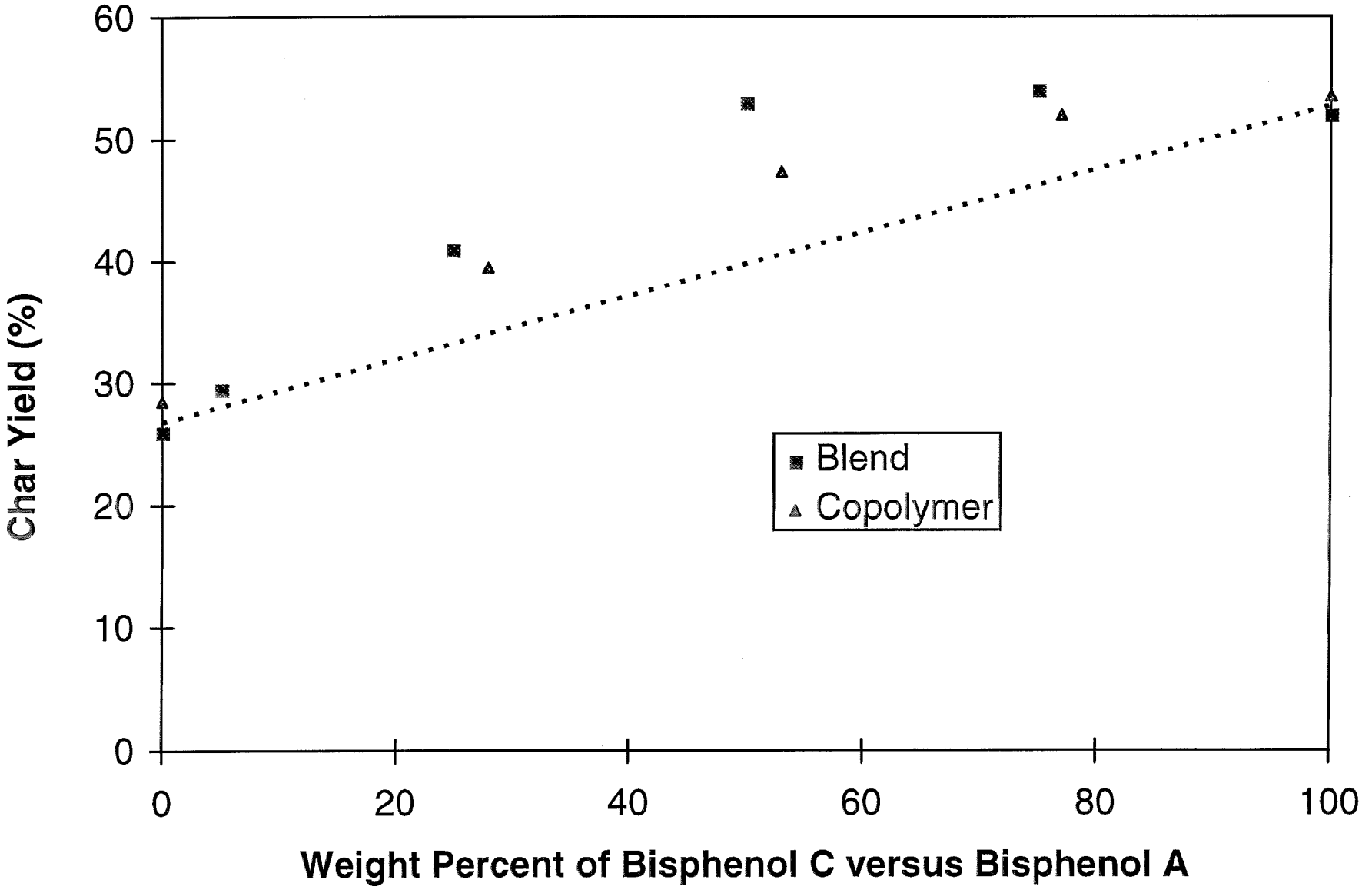
Polyarylate Copolymers

BPC/BPA	Onset Decomposition (°C)[a]	Char Yield at 700°C (%)	Peak Mass Loss Rate (%/s)
100/0	410	50	0.067
75/25	416	50	0.056
50/50	419	48	0.080
25/75	423	37	0.18
0/100	469	25	0.29

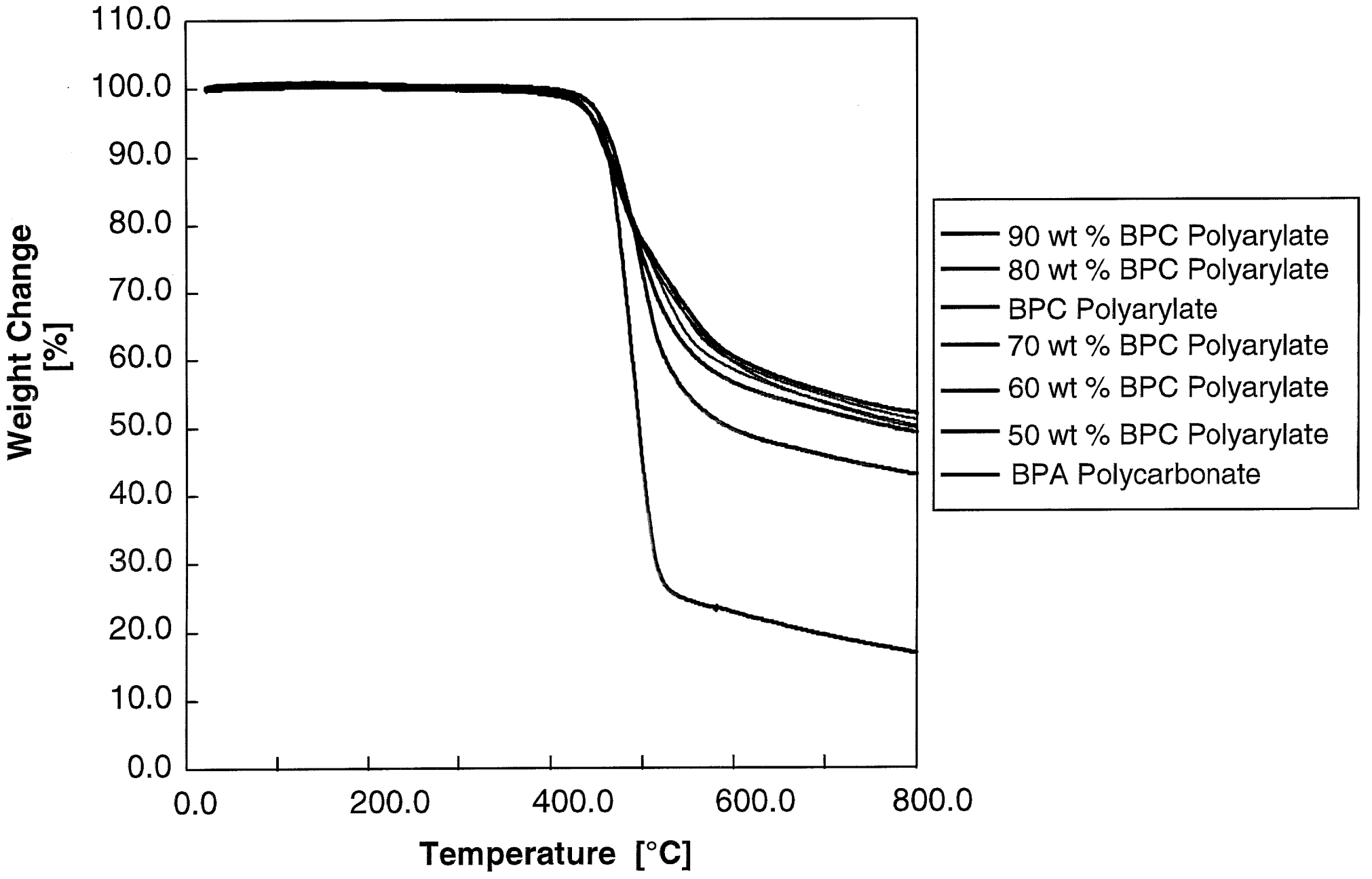
Blends with Polysulfone

	Onset of Decomposition (°C)	Char at 700°C (%)	Rate of Mass Loss (%/s)
bisphenol A polysulfone	476	33	0.33
50/50 wt% blend	403	50	0.088
BPC-Polyarylate	421	52	0.068

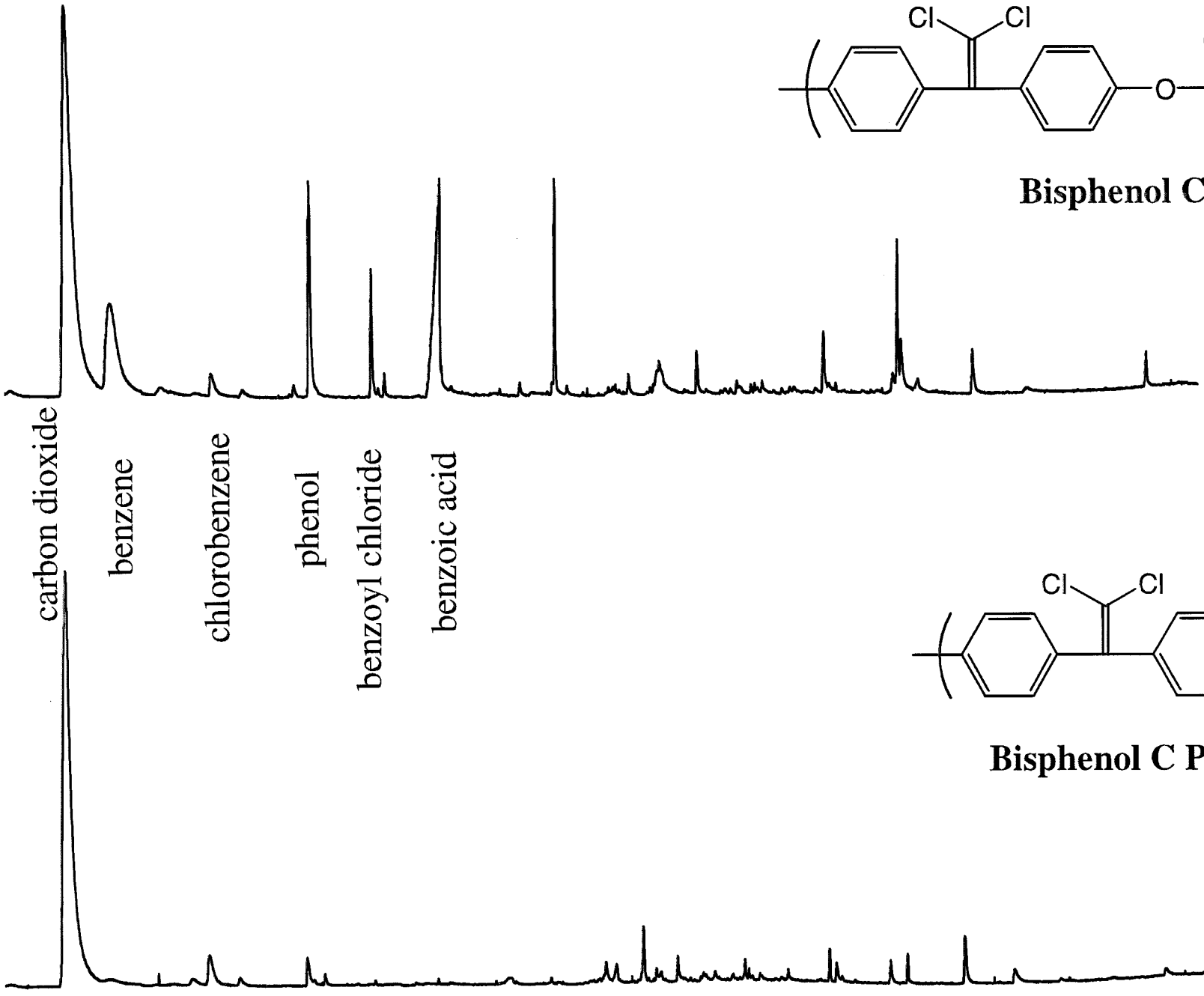
Enhancement of Char Yield

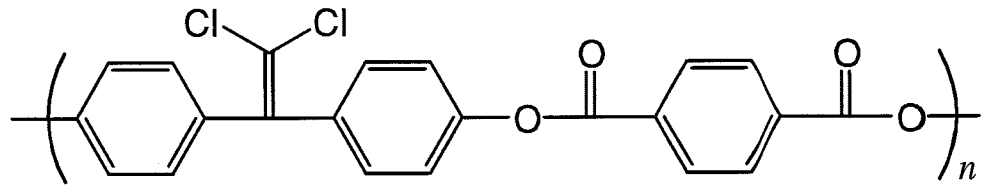


Blends of BPC-Polyarylate with BPA-Polycarbonate

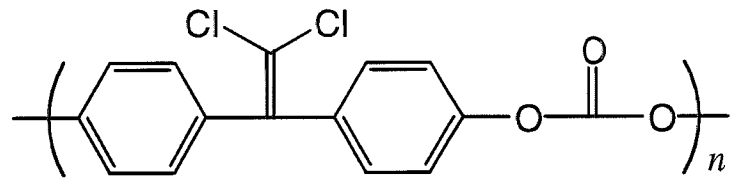


Decomposition Products For Bisphenol-C-Based Polymers



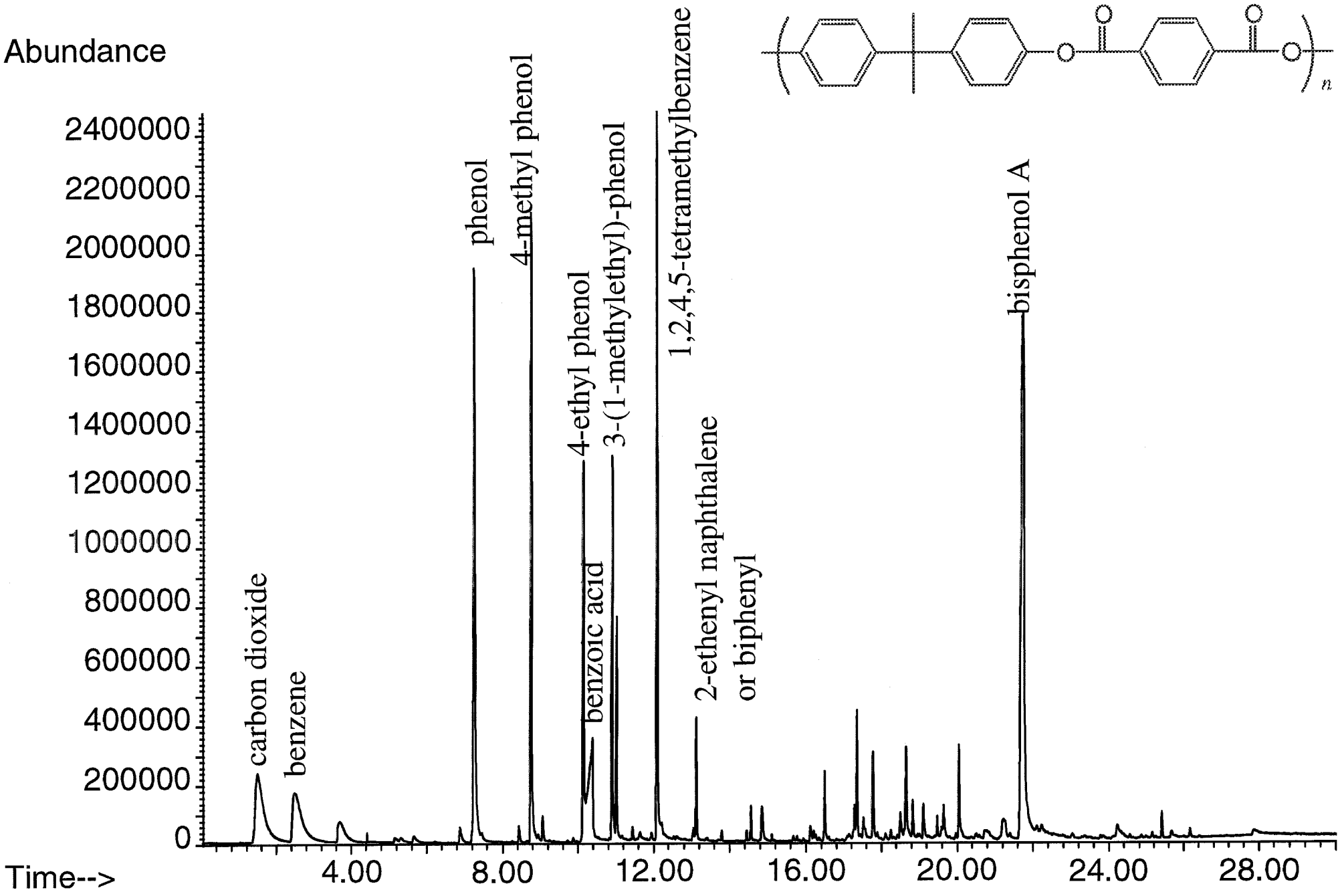


Bisphenol C Polyarylate

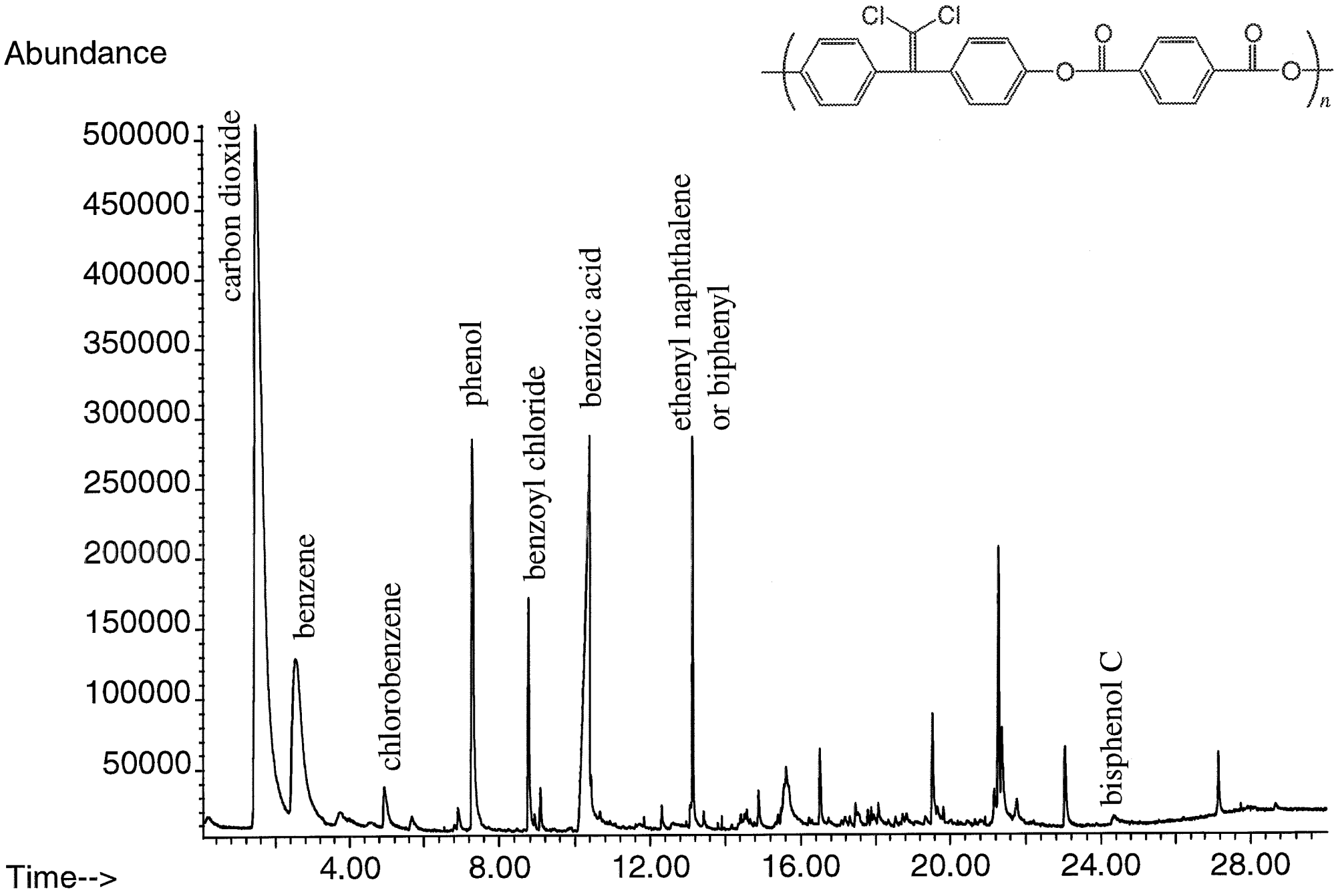


Bisphenol C Polycarbonate

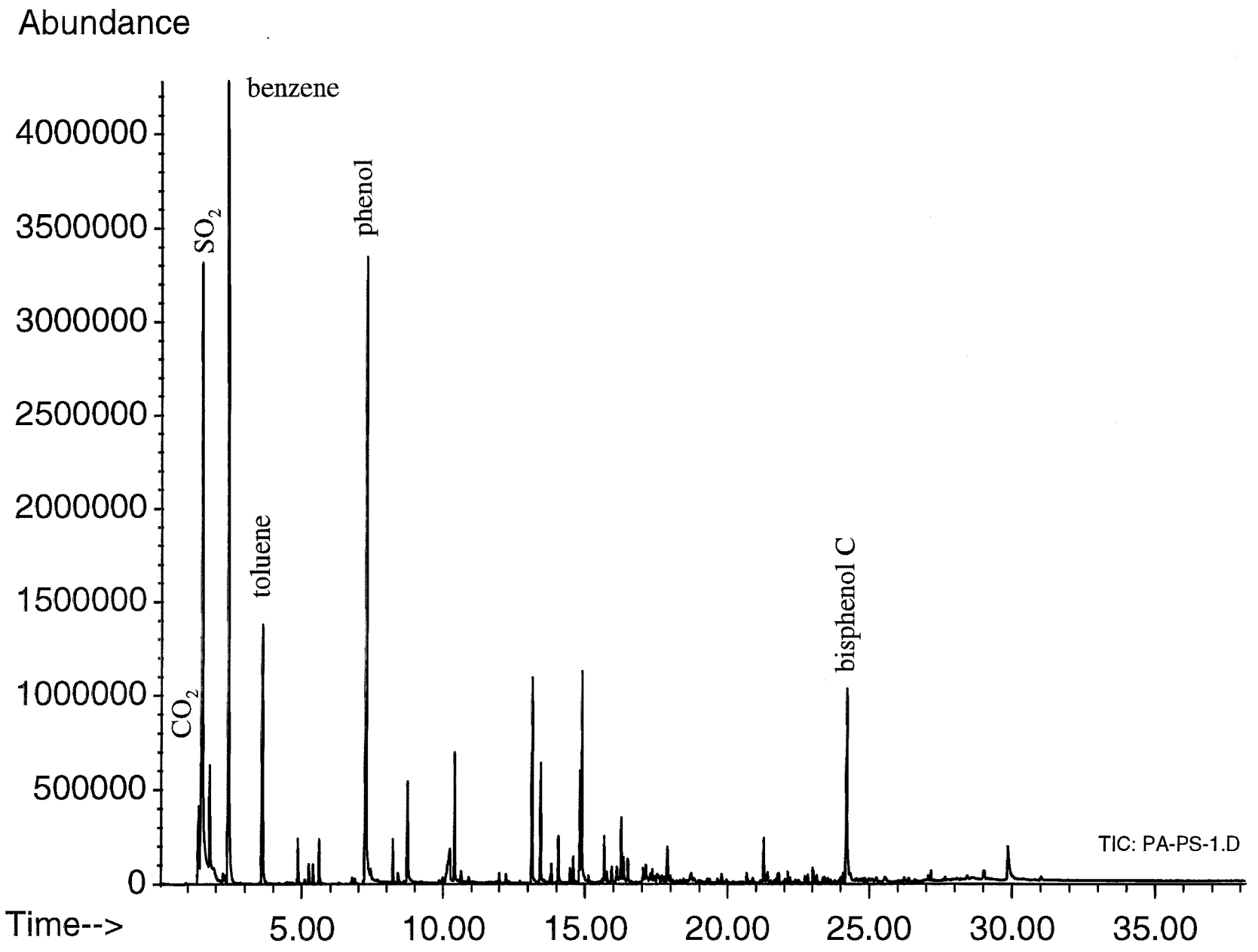
Decomposition Products From Bisphenol A Polyarylate



Decomposition Products From Bisphenol C Polyarylate



Decomposition Products From Blend



50/50 wt% Polysulfone/BPC-Polyarylate Blend

Microcalorimetry of Bisphenol C Based Materials

Sample	HR Capacity (J/g-K) (deconvoluted)	Total HR (kJ/g)
BPC-S8-PE	251	19.2
DPE-BPC	180	17.0
BPC	129	11.9
BPC-S2-PE	101	8.5
BPC-PC	51	7.4
BPC-PA	29	5.5
BPC-Br-PA	26	3.5
BPC-N-PA	26	4.4
T-PA	18	6.3

Other Poly: Microcalorimetry of Polyarylates

Sample	HR Capacity (J/g-K) (deconvoluted)	Total HR (kJ/g)
BPA-PA	486	22.4
S-PA	158	14.7
4ClBPA-PA	124	7.7
BPAF-PA	83	6.2
4BrBPA-PA	71	6.1
BPC-PA	29	5.5
T-PA	18	6.3

Flame Suppressing Polyhydroxyamides and Derivatives

Jungsoo Kim and Simon. W. Kantor

This section of the Cluster F project deals with the synthesis, characterization and flame suppressing behavior of polyhydroxyamides (PHA) and their derivatives. The principal derivatives that have been investigated include brominated, fluorinated and phosphorous containing polymers. In addition, in order to confirm the cyclization chemistry of the PHA's, appropriate model compounds were also prepared and studied. It was shown that the PHA's will cyclize when heated above 200 °C to liberate small flame quenching molecules and transform into polybenzoxazoles (PBO) which are flame resistant and generate large amounts of char.

There were no University of Massachusetts graduate students working on this part of the project from late 1995 to 1999. The following personnel were involved:

Dr. Chunping Gao Post-Doctoral Fellow 10/95-12/96
Ph.D 1995, McGill U.

Dr. Doohyun Baik Post-Doctoral Fellow 2/97-2/98
Associate Professor and Visiting Scientist
Chungnam National U.(Korea)

Mr. Haeyoung Kim Visitng Graduate Student 8/97-2/98
Chungnam National U.(Korea)

Dr. Jungsoo Kim Post-Doctoral Fellow 9/98-Present
Ph.D 1996, U. of Akron

Most of the disclosures and publications pertaining to this work were made in internal CUMIRP reports. One external publication and presentation was made:

Gao, C.; Kantor, S. W. *Synthesis of Precursor Flame Suppressing Polymers*. Proc. 54th Annual Technical Conference, USA Soc. of Plastics Engineers, Indianapolis, IN. May 1996, P. 3072.

A second publication is in preparation:

Kim, J; Kantor, S. W. *Synthesis, Characterization and Cyclization of Aromatic Polyamides Containing Pendant Phosphate or Phosphonate Groups*. To be submitted to the Journal of Polymer Science.

PHA's and many of their derivatives have been described in the patent literature. Earlier disclosures have also been made for their use in coatings, wire insulation, photoresists and composites. However, their flame retardant behavior has not been studied in these applications nor have their uses been well documented or characterized. These areas of research still constitute highly worthwhile objectives. A particular fruitful investigation which has been initiated involves aqueous processing of PHA's from alkaline solutions to form PHA and PBO fibers and films. This processing method will provide an environmentally clean route to desirable PBO products.

March 7, 2000

Flame Retardant Precursors to Heterocyclic Polymers

Jungsoo Kim and Simon W. Kantor

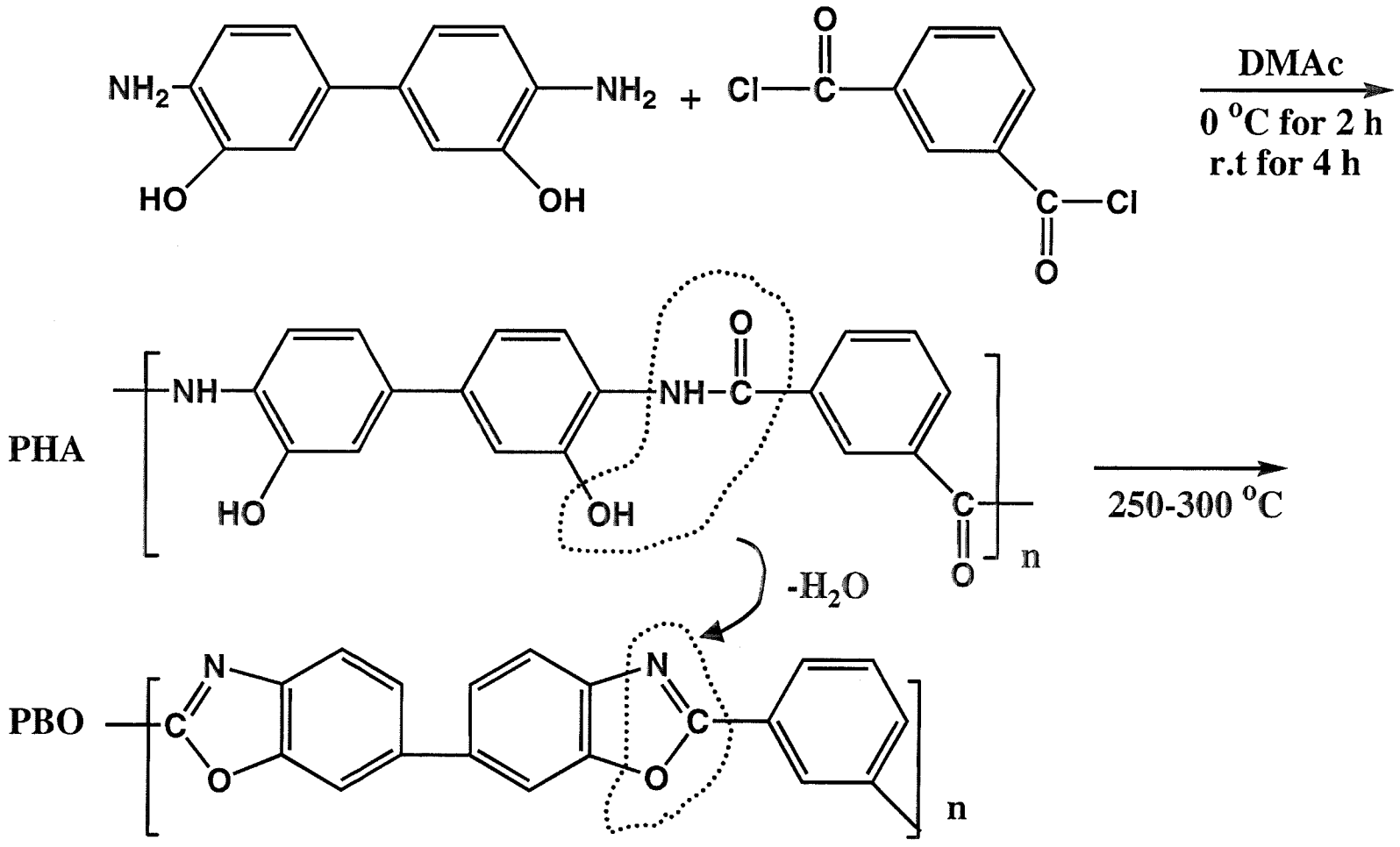
University of Massachusetts
Amherst, MA

Principal Objectives

- **Investigate New Concepts for Flame-Retardant Polymers**
- **Facilitate Processing of Rigid Rod, High Temperature Polymers in Precursor State**
- **Investigate Potential Applications in Fibers, Coatings and Films**

Polyhydroxyamide (PHA)

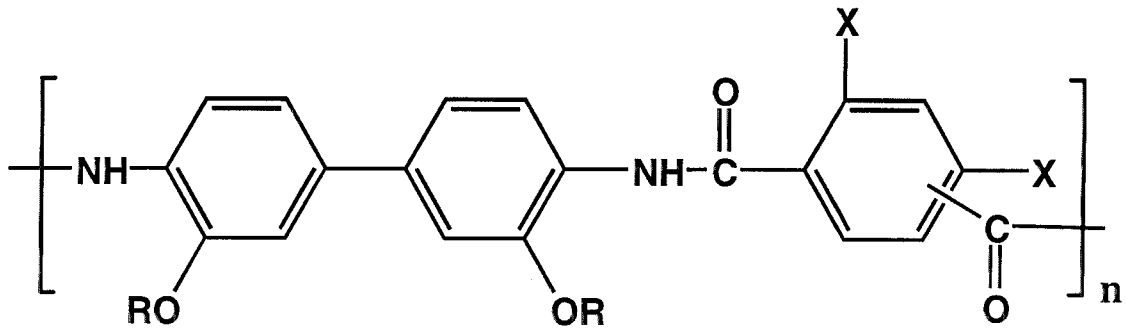
Precursor to Polybenzoxazole (PBO)



Precursor Polymers

- High Molecular Weights
- Processable, Soluble
- Large Endothermic Cyclization to PBO
- Simultaneous Release of Flame Quenching Molecules which Assist in Fire Retardancy
- PBO: Stable High Temperature Polymer
  - Low Flammability with Low Heat Release
  - High Char Yield
- Useful as Films, Fibers, Composites and Insulating Wire Enamels

Flame Retardant PHA's



$\xrightarrow{\Delta}$

PBO + ROH + X• Flame Quenching Molecules

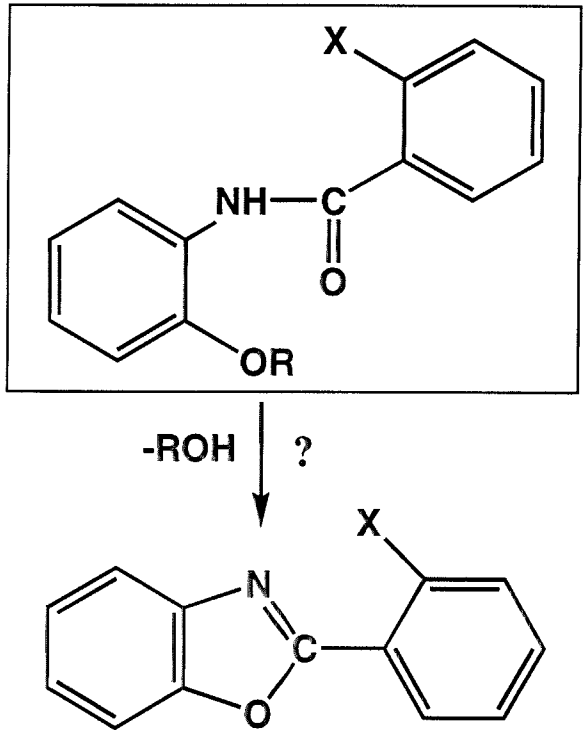
X = H, R = Phosphorous: $(C_6H_5)_2P{=}O$, $(CH_3O)_2P{=}O$, $(C_6H_5O)_2P{=}O$, $(C_6H_3Cl_2O)_2P{=}O$

X = H, R = Acyl: $COCH_3$, $COCF_3$

X = H, R = Alkyl: CH_3, CF_3

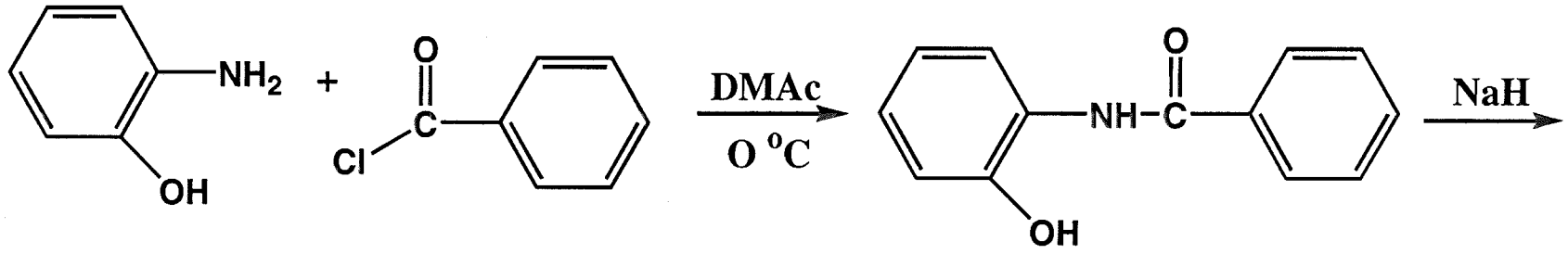
X = Br, R = H

Model Compounds



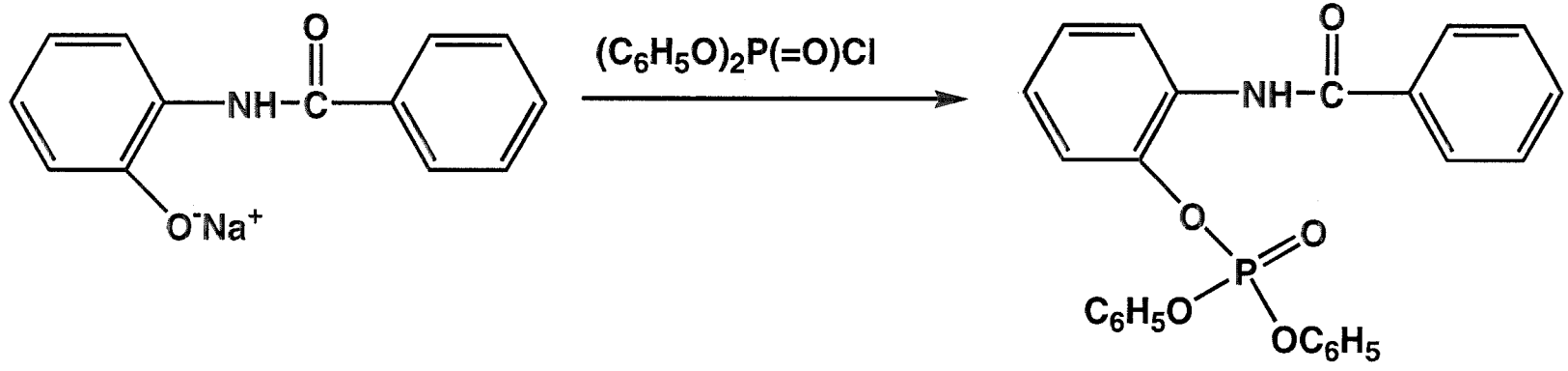
Type	OR	X
Phosphorous	$OP(=O)(OCH_3)_2$	H
	$OP(=O)(OC_6H_5)_2$	H
	$OP(=O)(OC_6H_3Cl_2)_2$	H
	$OP(=O)(C_6H_5)_3$	H
Acyl	$OC(=O)CH_3$	H
	$OC(=O)CF_3$	H
Alkyl	OCH_3	H
	OCF_3	H
Halogen	OH	Br

Acyl and Phosphorous Derivatives



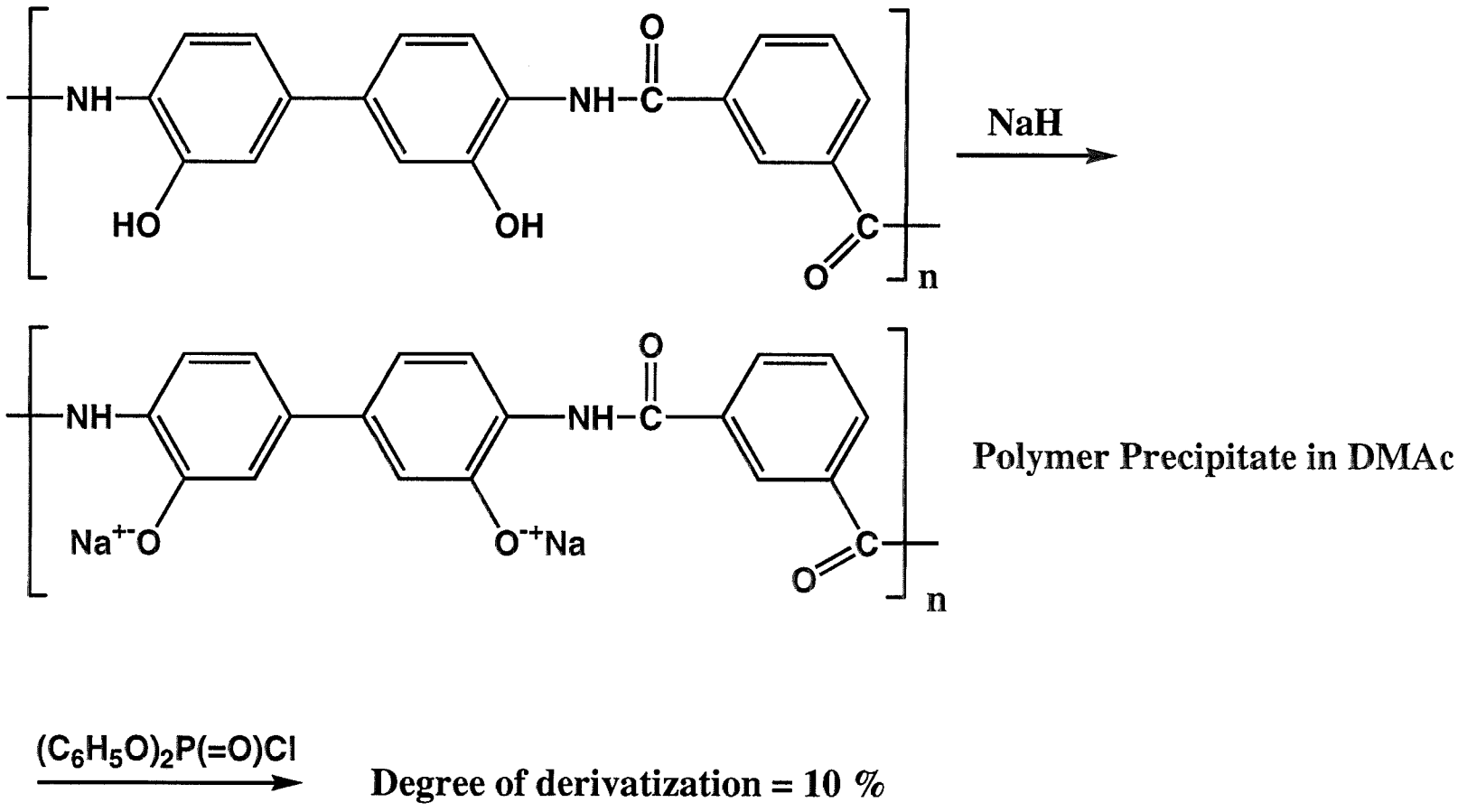
N-(2-hydroxyphenyl)benzamide

mp 169-170 °



N-(2-benzamidophenyl)diphenyl phosphate

mp 92-94 °


NH
NH
C
O
HO
OH
C
O
n
NaH
NH
NH
C
O
Na+-O
O-+Na
C
O
n
Polymer Precipitate in DMAc
(C6H5O)2P(=O)Cl
Degree of derivatization = 10 %

Improvement for the Derivatization

PHA Solution in DMAc

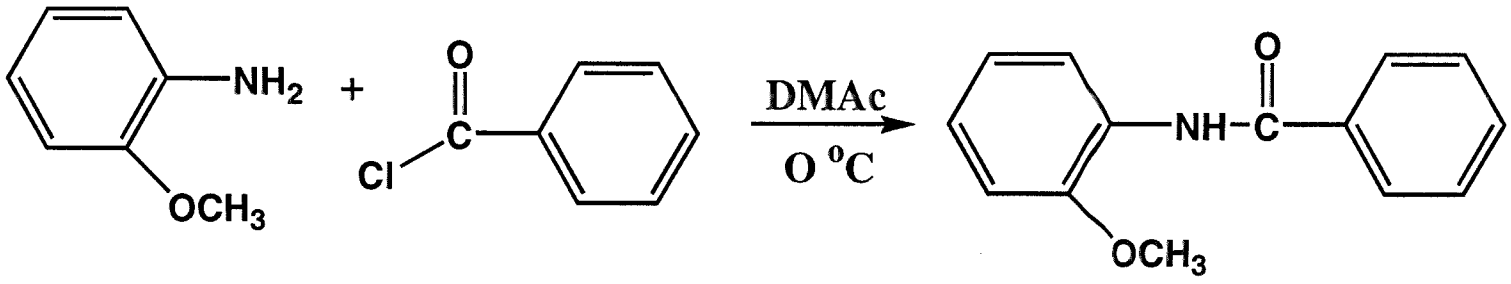
↓

15-20 % of $(C_6H_5O)_2P(=O)Cl$ in DMAc at 100 ^{o}

↓

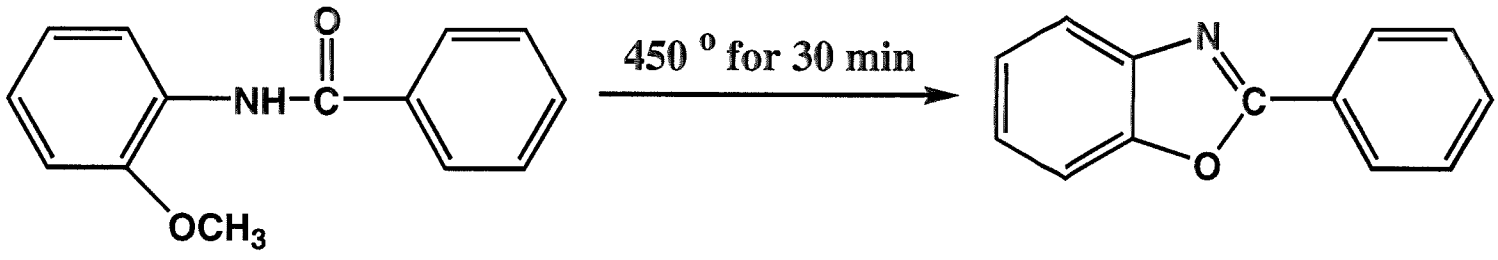
Degree of Derivatization = 67 %

Alkoxy Derivatives

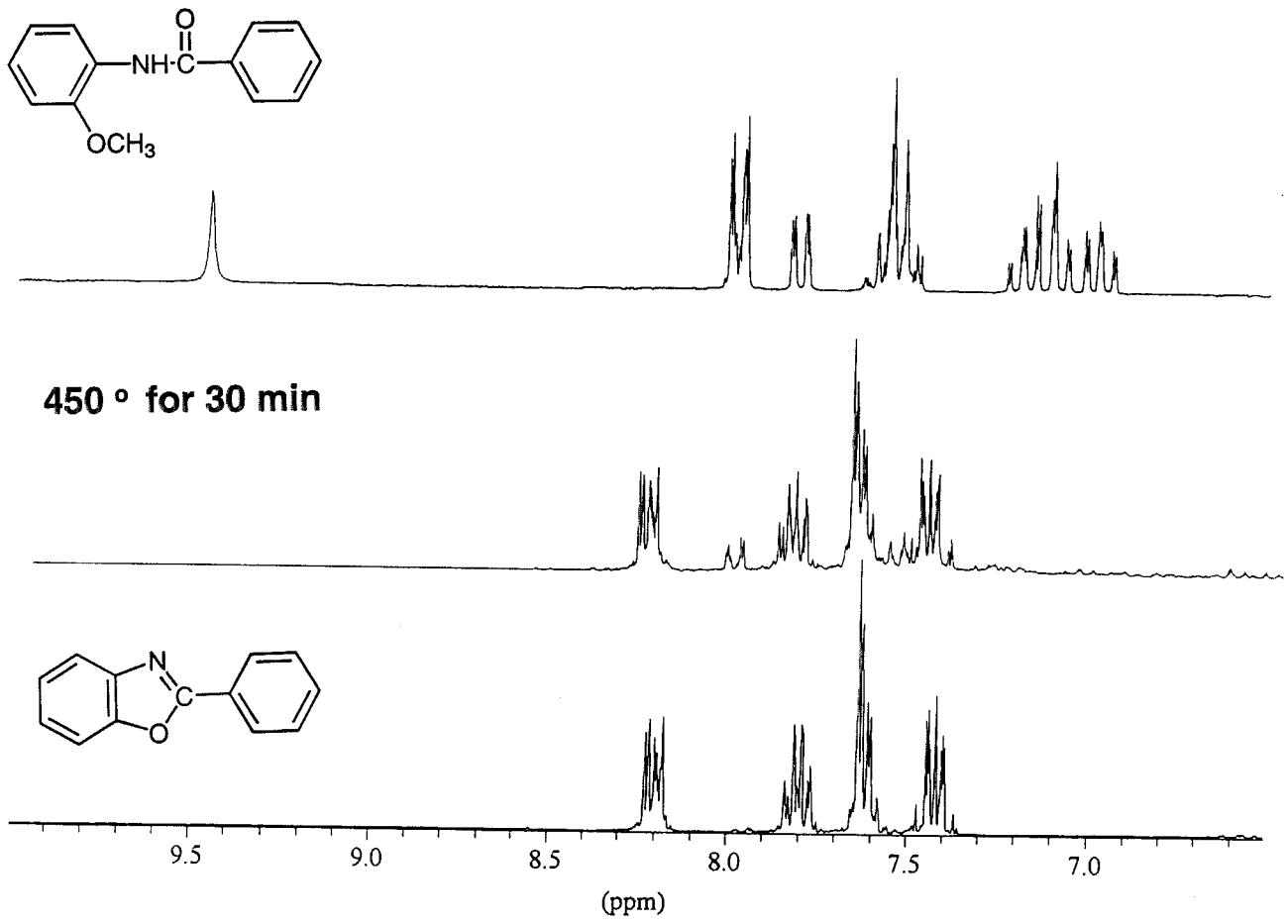


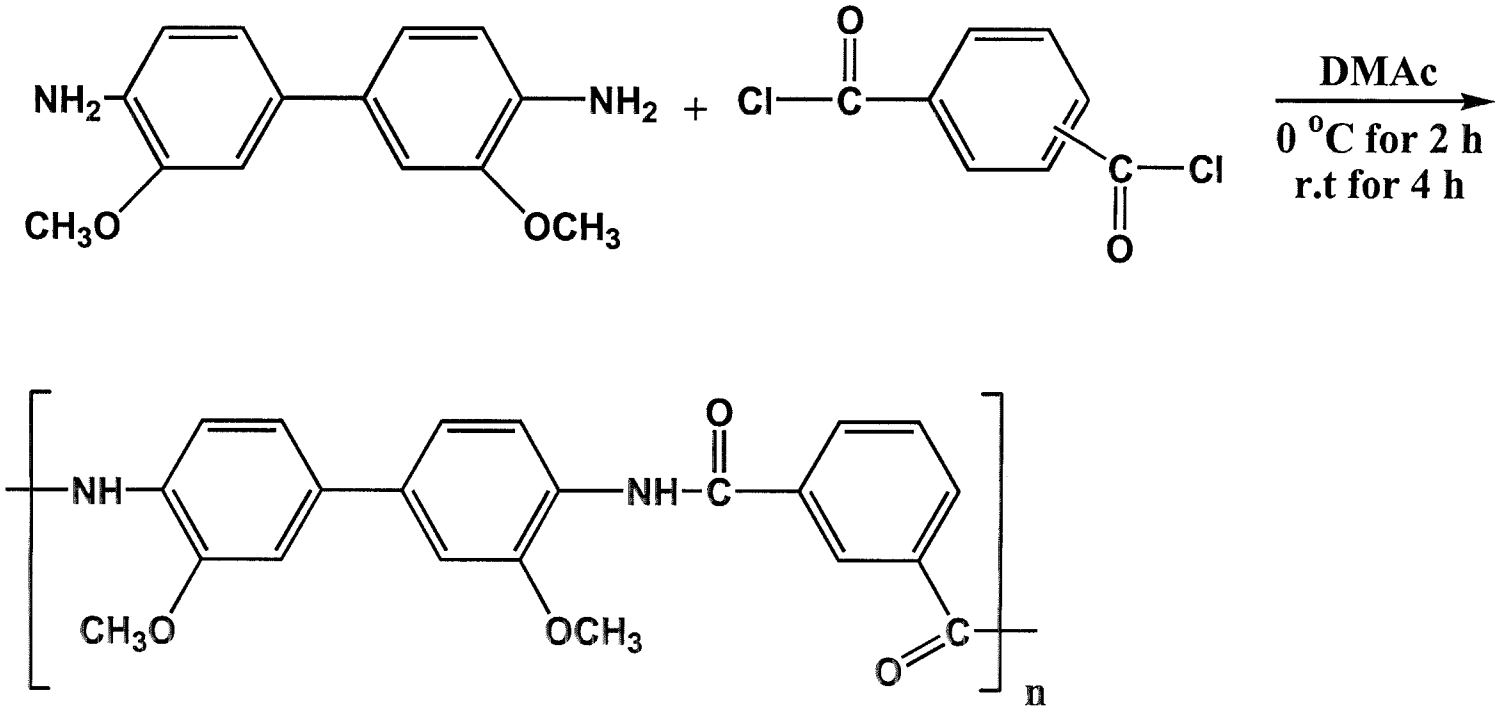
N-(2-methoxyphenyl)benzamide
mp 66-67 °

Cyclizes at High Temperature



Thermal Cyclization of N-(2-Methoxyphenyl) Benzamide



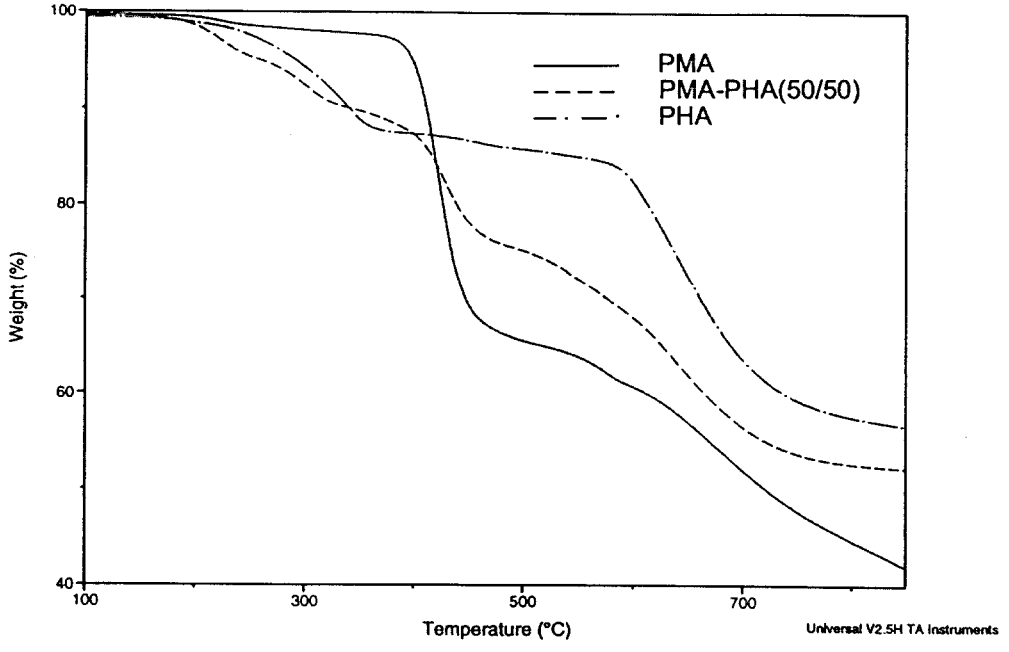


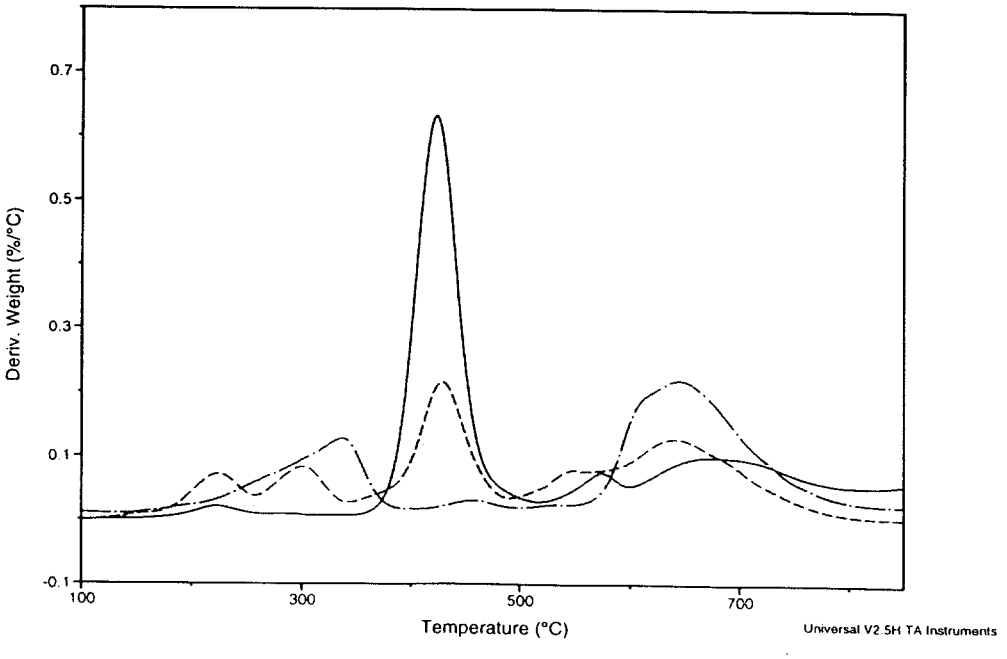
Poly(3,3'-dimethoxy-4,4'-biphenylene isophthalamide) (PMA)

PMA Solubility

		Solubility							
Code	Viscosity (η_{inh})	NMP	DMSO	DMF	Pyridine	THF	Acetone	MeOH	$CHCl_3$
PMA	0.62	++	++	++	++	-	-	-	-
PMA-PHA(50/50)	0.70	++	++	++	-	-	-	-	-
PHA	0.60	+	+	-	-	-	-	-	-
		++ (LiCl)	++ (LiCl)	++ (LiCl)					

TGA and DTG Curves in N_2

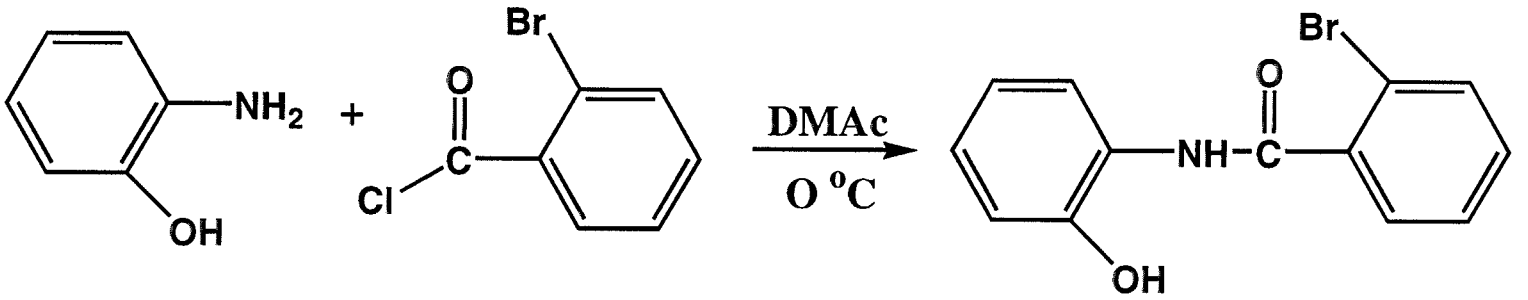




Thermal Properties

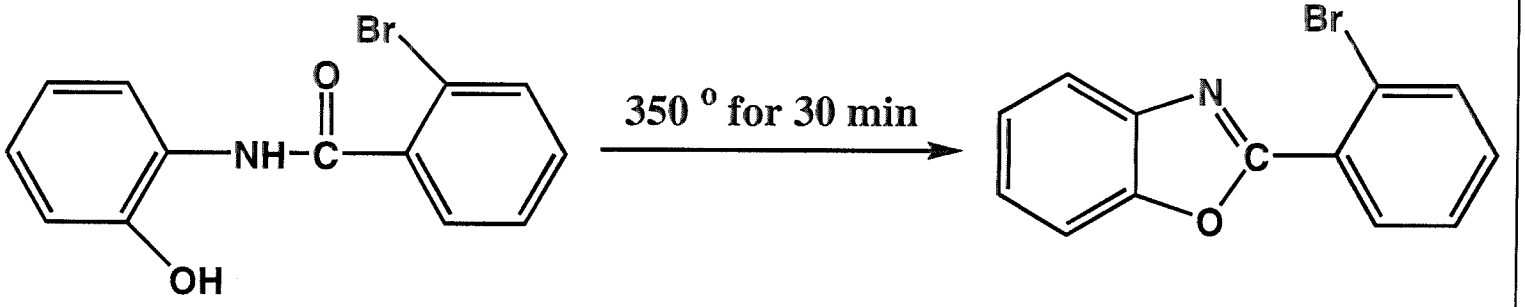
Polymer Code	Residual Weight (%)			Weight Loss (°C)		
	400 °C	700 °C	850 °C	20 %	30 %	40 %
PMA	95	52	42	427	445	612
PMA-PHA (50/50)	87	56	52	436	568	659
PHA	87	63	57	612	661	736

Halogen Derivatives

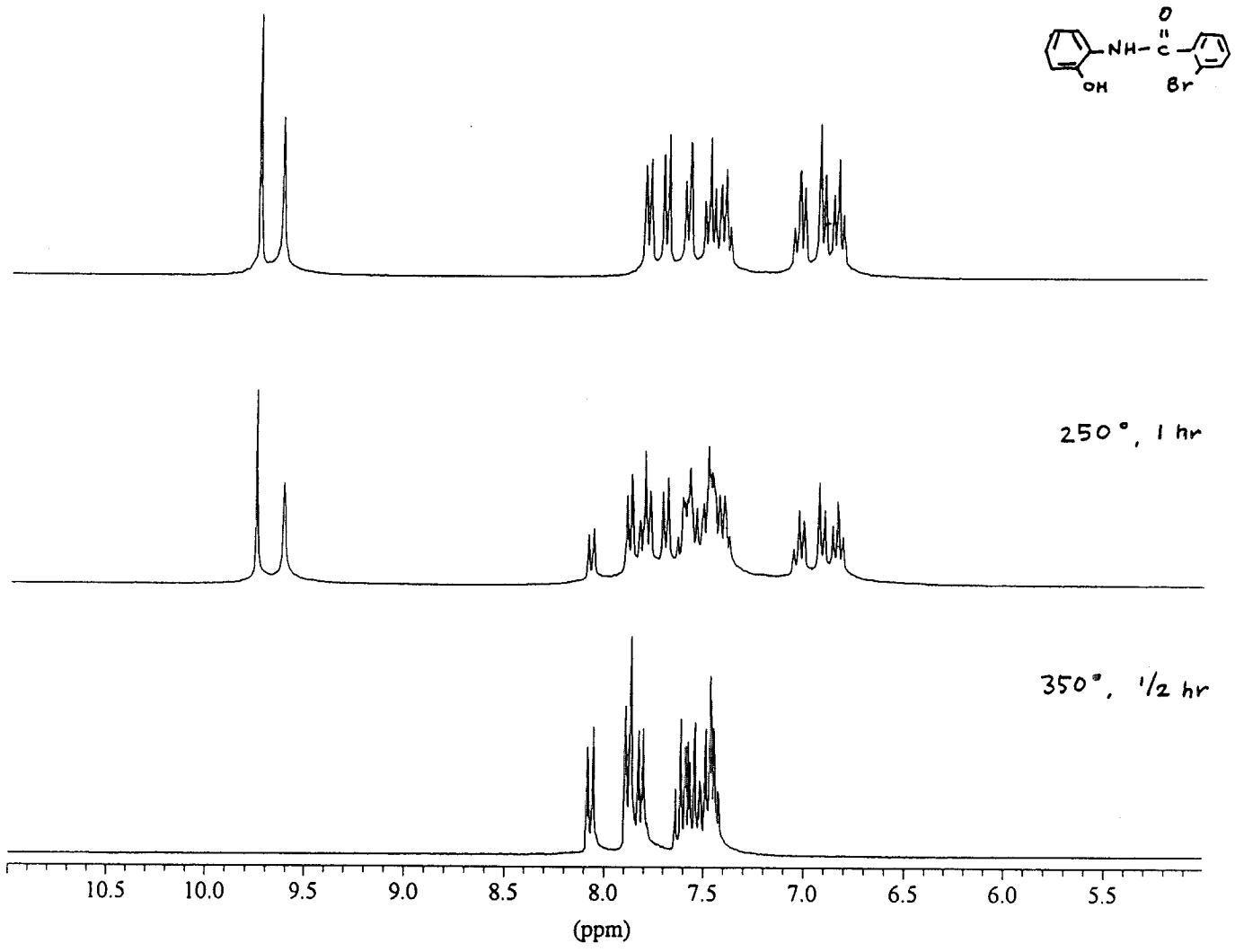


N-(2-hydroxyphenyl)-2-bromobenzamide

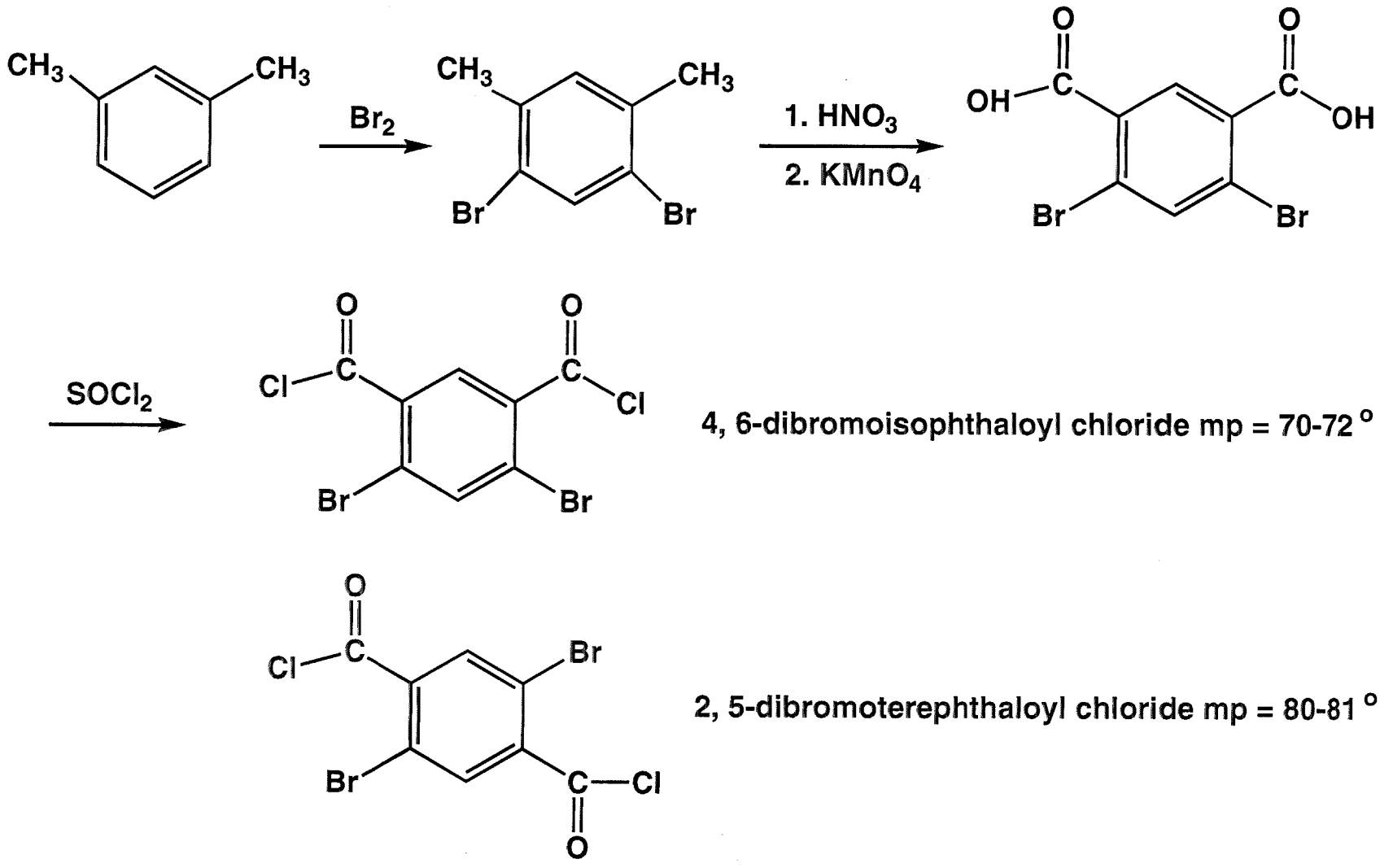
mp 183-184 °



Thermal Cyclization of N-(2-hydroxyphenyl)-2-bromobenzamide



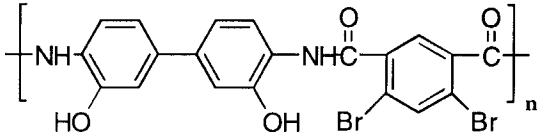
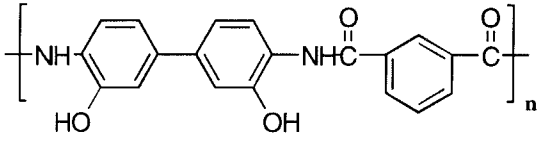
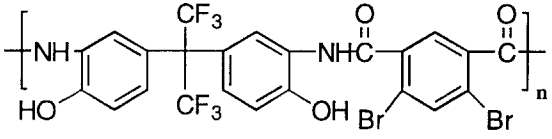
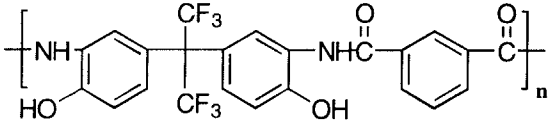
Monomer Preparation



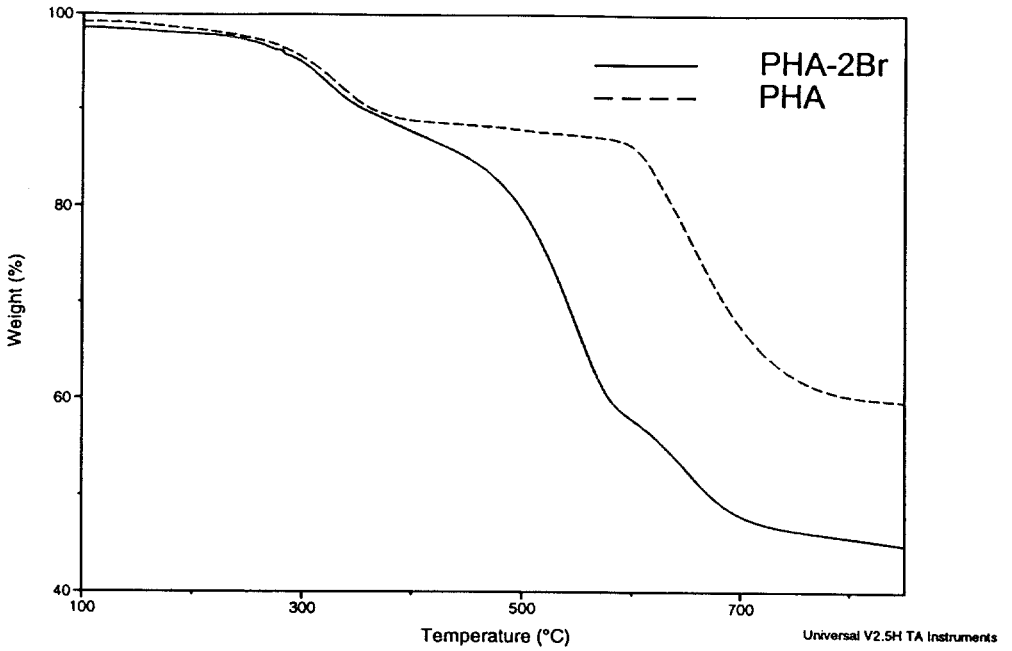
4, 6-dibromoisophthaloyl chloride mp = 70-72 °

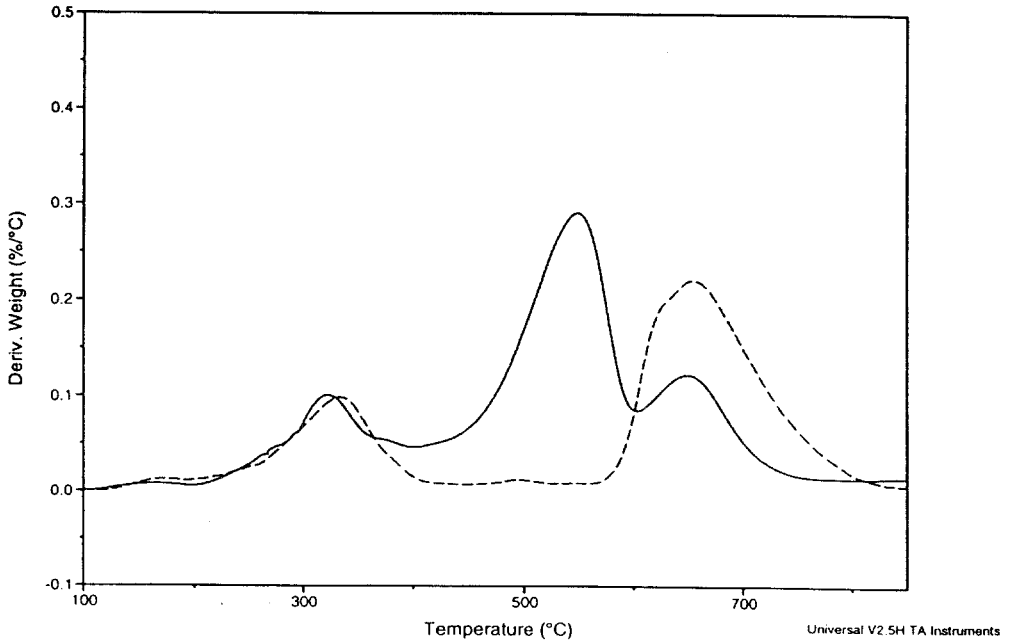
2, 5-dibromoterephthaloyl chloride mp = 80-81 °

Solubility of Halogenated PHA's

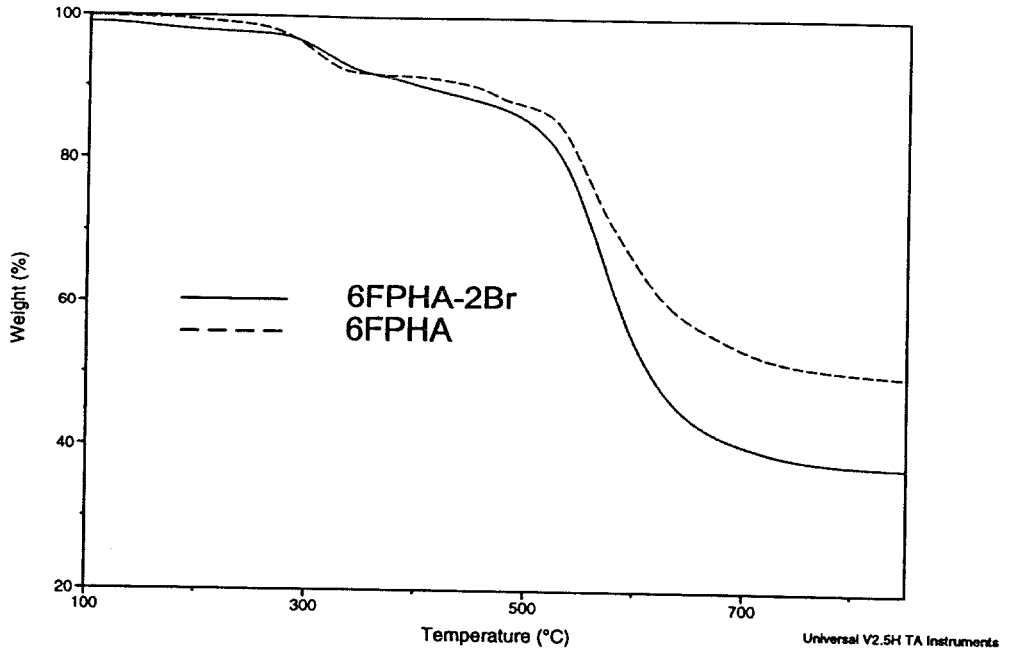
Polymer Structure	Polymer Code	η_{inh}	Solubility							
			NMP	DMSO	DMF	Pyridine	THF	Acetone	MeOH	$CHCl_3$
	PHA-2Br	0.49	++	++	++	+	-	-	-	-
	PHA	0.52	+	+	-	-	-	-	-	-
			++ (LiCl)	++ (LiCl)	++ (LiCl)					
	6FPHA-2Br	0.25	++	++	++	++	++	-	-	-
	6FPHA	0.23	++	++	++	-	++	-	-	-

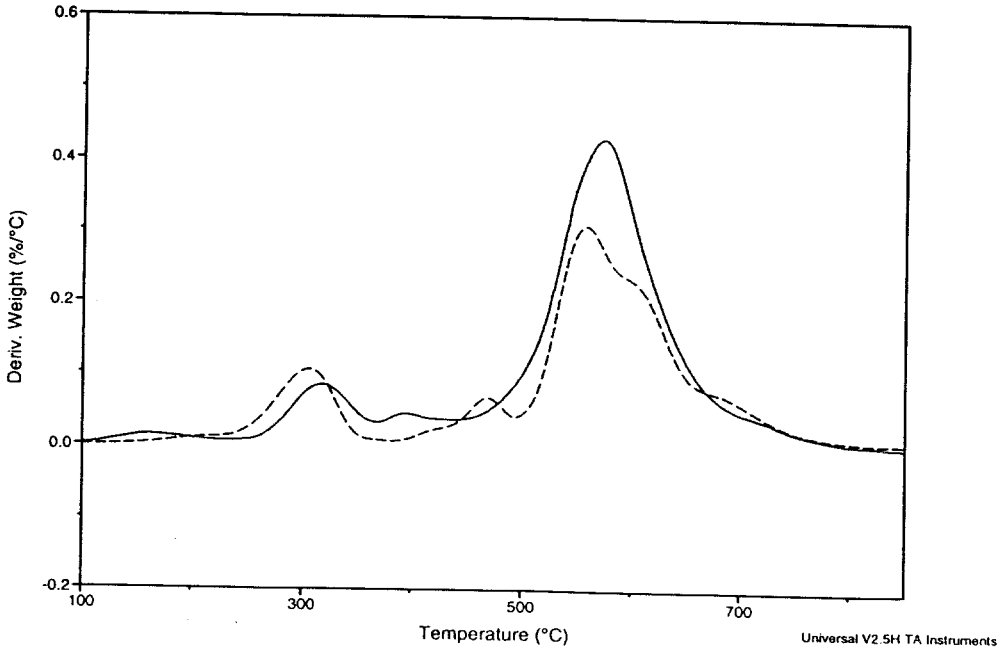
TGA and DTG Curves in N_2



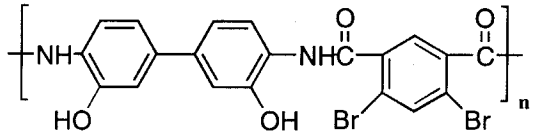
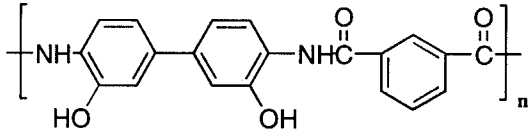
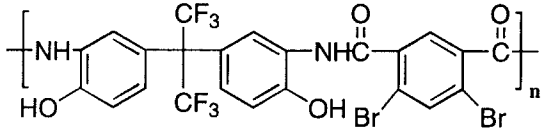
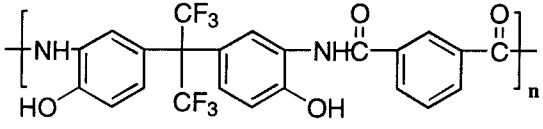


TGA and DTG Curves in N_2

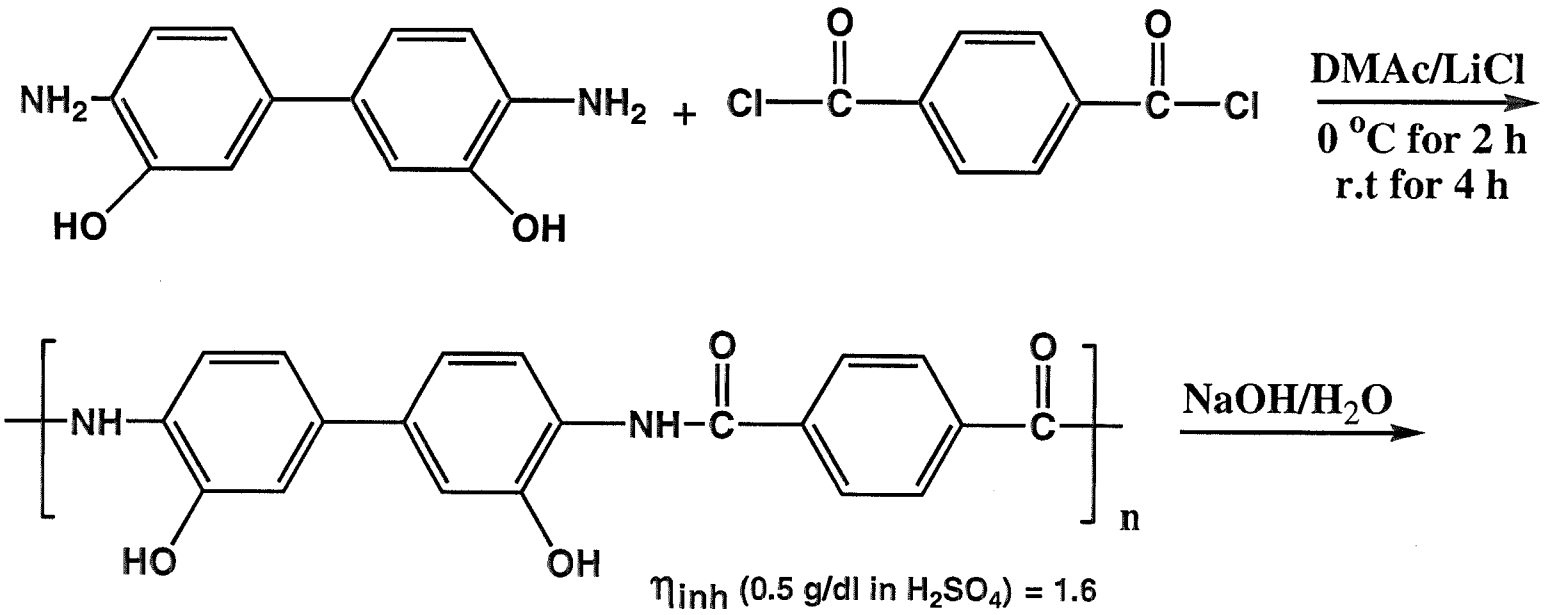


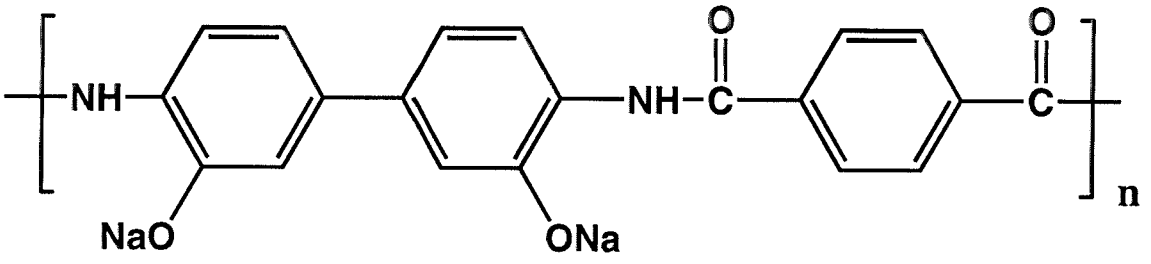


Thermal Properties

Polymer Structure	Polymer Code	Residual Weight (%)			Weight Loss (° C)		
		400 °C	700 °C	850 °C	20 %	30 %	40 %
	**PHA-2Br**	86	46	43	487	535	571
	**PHA**	86	64	57	622	669	740
	**6FPHA-2Br**	90	40	37	533	565	585
	**6FPHA**	92	54	50	549	583	629

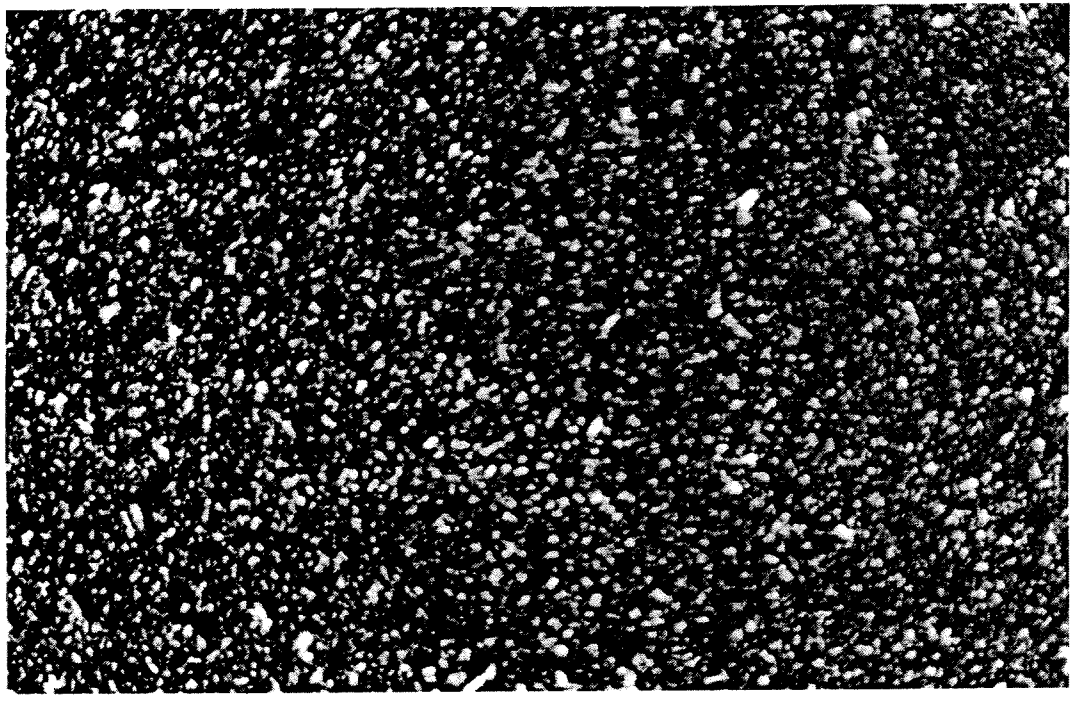
Liquid Crystalline PHA





Water Soluble
Liquid Crystalline PHA

PHA-Na



Photomicrograph of Tere-PHA Sodium Salts
(15 % in water), 100 x mag.

Conclusions

- Derivatized polyhydroxyamides

  - 57 % increase in phosphorous derivatization.
  - methoxy derivative cyclizes to PBO above 450 ^{o} and shows improved solubility.
  - brominated PHA's were prepared and shown to release Br before PBO decomposition.

- High M.W. tere-PHA was prepared and its sodium salt was soluble in water. At high concentration (> 15%) it was liquid crystalline.

New Objectives

- Test Fiber Spinning of Liquid Crystalline PHA
- Investigate the Potential of PHA as Wire Enamel for Copper
- Investigate the Potential of PHA Unsaturated Derivatives for High Temperature Photoresists

  R = acryloyl, methacryloyl, cinnamoyl

New Results from Milligram-Scale Polymer Flammability Experiments

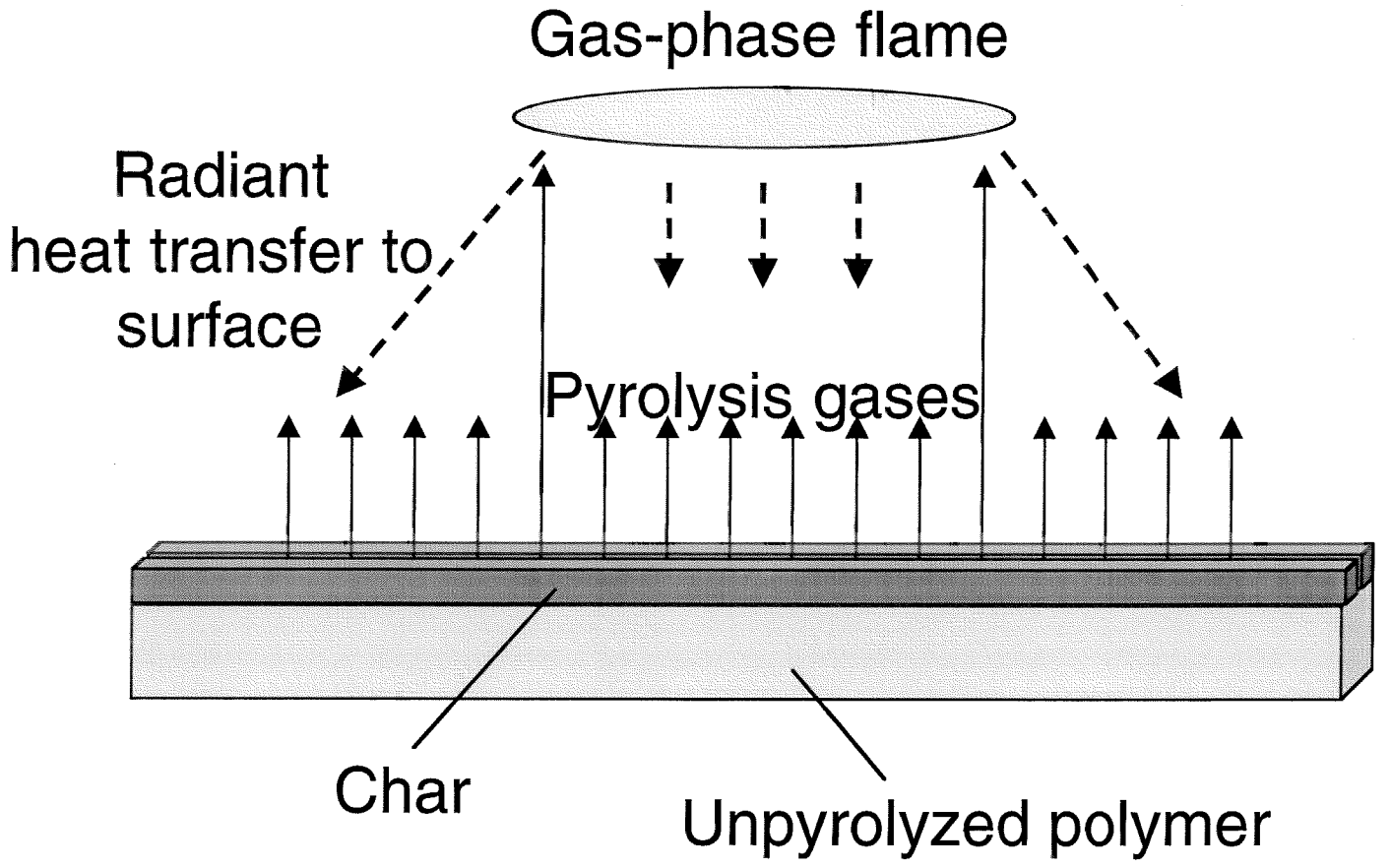
Phillip R. Westmoreland[a], Huiqing Zhang[a,b], Jessie Ip[a]

[a]Chemical Engineering Dept, UMass Amherst
[b]Polymer Science and Engineering Dept, UMass Amherst

Today, focus on test methods.

- One goal of our work is quantitative reaction mechanisms for polymer combustion, developed using data and computational chemistry
- Micro-scale tests of flammability:
  - FAA microcalorimeter
  - Hybrid TGA/DSC/GC-MS
  - **Pyroprobe GC-MS**

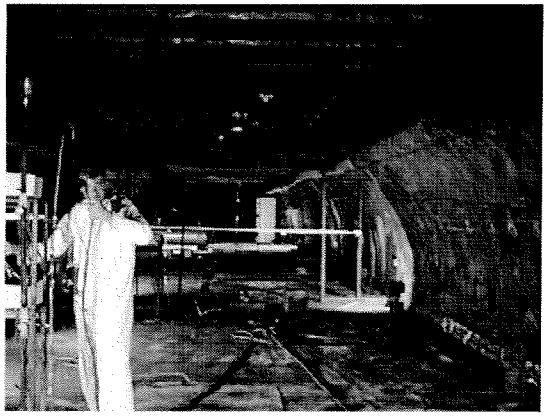
To make fire-safe polymers, understand polymer pyrolysis.



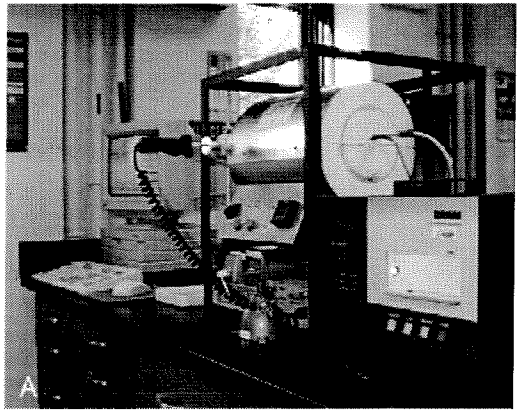
How to get more flame resistance?

- Avoid releasing combustible gases.
  - Use decomposition-resistant polymers.
  - Produce only char and inert gases.
- Slow the conductive heating of polymer.
  - Make insulating char layer.
  - Exploit endothermic phase transitions or decomposition.
- Suppress gas-phase ignition and flame propagation.
  - Release chemical fire suppressants (halogens, phosphates).

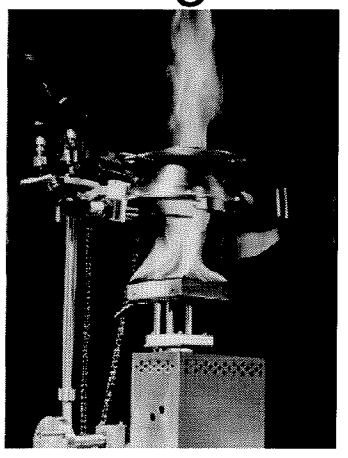
New flammability tests for mg.



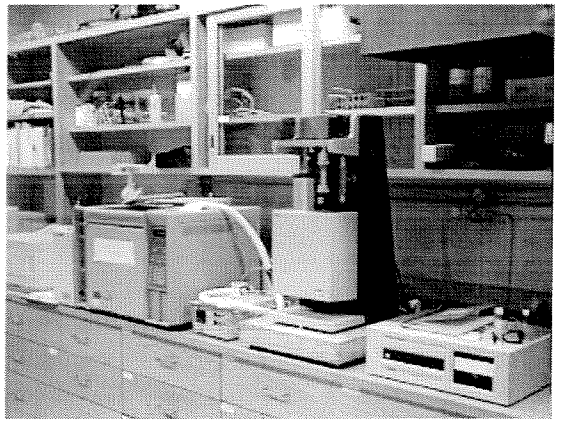
Aircraft: Big samples



FAA microcalorimeter: mg



Cone calorimeter: 100 g

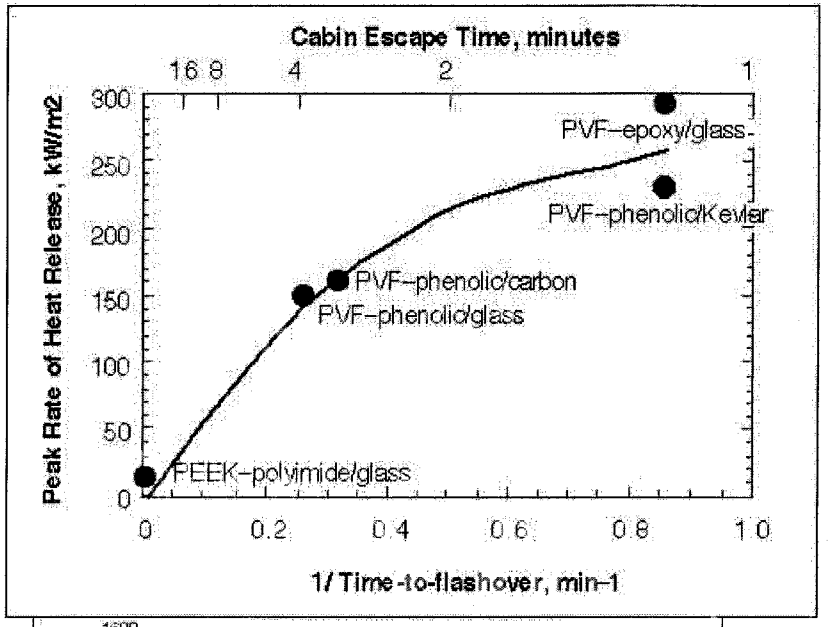


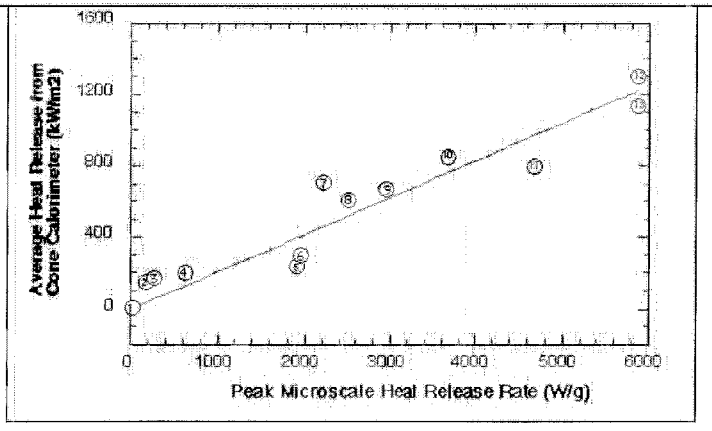
UMass TGA/DSC/GC-MS: mg

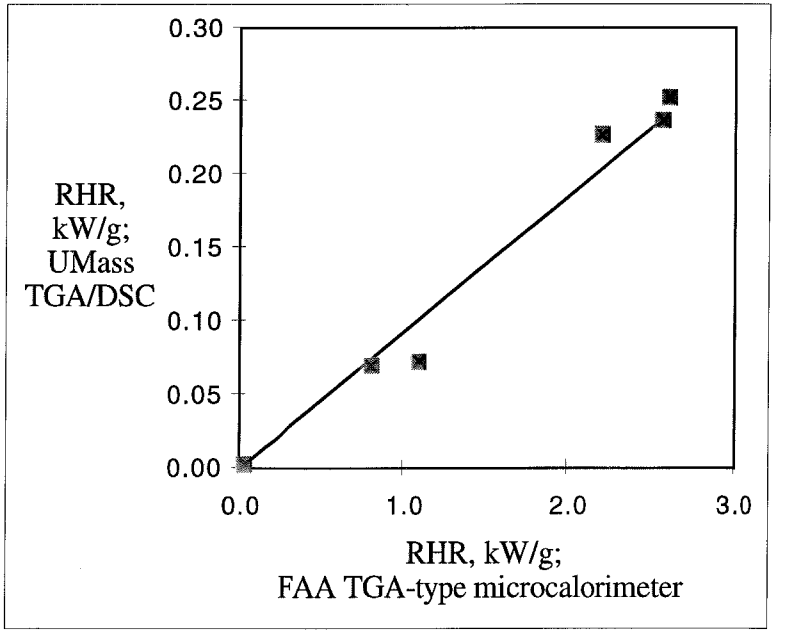
"Peak heat release rate" is a good correlating parameter.

- PHRR = Maximum value of pyrolysis gas's (evolution rate)·(heat of combustion)
- In cone calorimeter and FAA microcalorimeter, measure oxygen depletion to get PHRR by correlation.
- In UMass hybrid pyrolyzer, find decomposition rate and $\Delta H_{combustion}$ separately.

Establish correlations among tests.







A third method: Couple the flash pyrolysis to GC/MS.

- Pro: Measure HHR = $\Sigma\, n_i \cdot \Delta H_{combustion,i}$ with same reactor as FAA microcalorimeter
- Challenge: Identify products, calibrate concentrations, and obtain $\Delta H_{combustion,i}$
- Con: Must get <u>all</u> species into GCMS; one-shot sampling (not continuous)

Typical conditions, procedure:

- Ramp to 750 or 1200°C at 5 or 10°C/ms
- Keep interface at 280°C
- Sample; separate with long, wide-bore DB-5 capillary column:
  - 36°C for 2-6 min
  - 36->295°C at 10°C/min
  - Hold for 30 min
- As peaks elute, collect mass spectra for 75 eV ionization
- Identify with spectrum analysis techniques and HP software
- Convert to relative mole fractions using relative ionization cross-sections

Typical product results: PEEK

$-C_6H_4-O-C_6H_4-O-C_6H_4-(C=O)-$

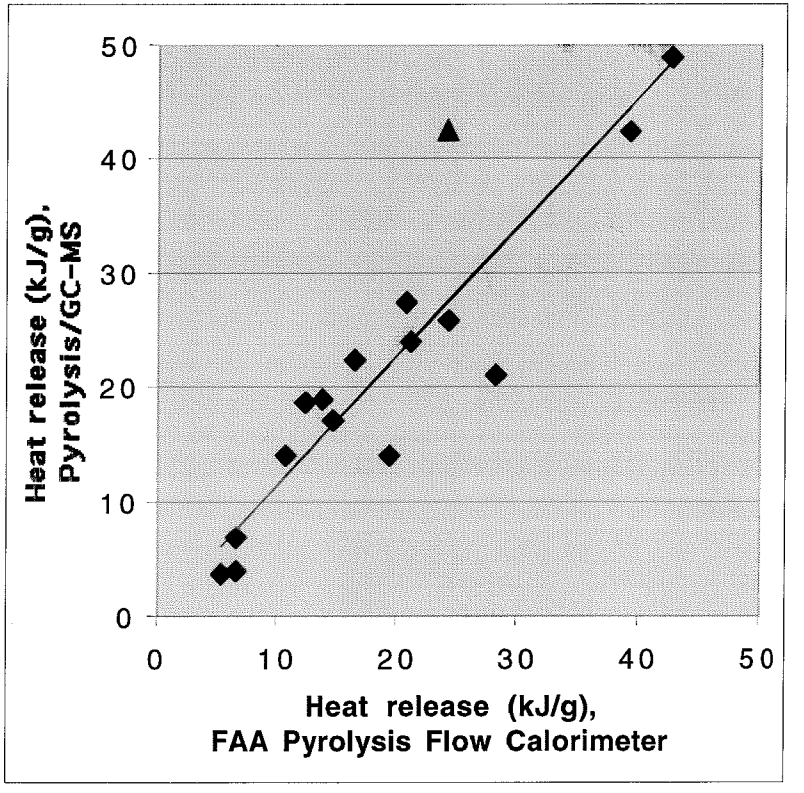
Mole fractions in the sampled gas	Sample 1		Sample 2	
	10°C/ms	5°C/min	10°C/ms	5°C/min
	to 1200°C	to 1200°C	to 1200°C	to 1200°C
CO2, carbon dioxide	0.102		0.321	0.237
C5H6, cyclopentadiene	0.048		0.041	
C6H6, benzene	0.325	0.086	0.233	0.060
C7H8, toluene	0.017		0.011	
C6H6OH, phenol	0.342	0.869	0.297	0.638
C10H8, naphthalene	0.055		0.043	
C6H5C6H5, biphenyl	0.031		0.012	
C6H5OC6H5, diphenyl ether	0.019	0.016	0.009	0.014
C12H8O, dibenzofuran	0.063	0.028	0.034	0.024
C12H10O2				0.015
1,4 diphenyloxybenzene				0.008
C25H18O3				0.005
Heat release, kJ/g sample	24.40	22.8	21.1	22.7

Detailed comparison shows T_{max} and heating rate effects.

Polymers	% Char yield by by TGA, 10°C /min to 930°C	% Char yield by PFC	Heat release determined from Pyroprobe/GC-MS				Pyrolysis Flow Calorimeter HR (kJ/g)
			At 10°C/ms (kJ/g gas)		5°C/s (kJ/g gas)	P/GC-MS HR at 1200°C (kJ/g)	
			750°C/20s	1200°C/30s	1200°C/30s		
PS	0.0%	0.0%	42.5	42.2	42.4	42.3	39.2
PMMA	0.0%	0.0%	25.9		25.9	25.9	24.3
P(a-me-Styrene)	0.0%	0.0%	41.5	36.4	42.5	39.5	24.2
Nylon 66	0.0%	0.0%	23.5	29.3	21.1	25.2	28.2
POM	0.0%	0.0%	19.0	19.0	19.0	19.0	13.9
PE	0.0%	0.0%	47.5		48.9	48.9	42.7
PBT	0.0%		27.6	29.7	32.2	30.9	
PET	0.0%	5.2%	25.1	27.4	22.4	24.9	16.6
PES	37.8%	28.1%	19.0	35.7	22.5	18.1	19.4
PC	11.5%	18.3%	29.0	27.6	27.2	24.2	21.2
PPO	21.2%	24.2%	36.0	32.4	35.9	26.9	20.8
Kevlar	31.8%	36.1%	24.1	25.9	25.1	17.4	14.8
PI	41.4%	51.9%	8.4	8.3	11.9	5.9	6.6
PEEK (PEK)	45.5%	52.9%	-	30.3	29.9	16.4	10.8
PEEK	44.8%	47.0%	33.2	37.6	34.0	19.7	12.4
PHA, 250C (PBO)	73.0%	69.5%	-	16.0	14.0	4.0	5.4
5%PHAA/PHA		32.4%	-	4.3	5.9	[3.4 w PFC char]	6.6

Mutual agreement => Validity and performance insights.

- Excellent agreement between the methods
- Main outlier is poly-alpha-methyl styrene; our number indicates same as polystyrene
- PES low – Char yield
- Nylon 6,6 low – unidentified species



This new approach complements our other methods.

- We demonstrated quantitative agreement.
- Detects the species generated in the FAA PFC test, although requiring more interpretation.
- Faster than TGA/DSC/GC-MS, although no time/temperature-resolved detail or DSC.

We gratefully acknowledge financial support of this work by CUMIRP Cluster F members.

ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF CHLORINATED BISPHENOL-BASED POLYMERS AND POLYCARBODIIMIDES AS INHERENTLY FIRE-SAFE POLYMERS

FEBRUARY 2000

JENNIFER R. STEWART,

B.S., UNIVERSITY OF MICHIGAN

Ph.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professors Richard J. Farris and Bruce M. Novak

Two different types of polymers were synthesized and their degradation and combustion behavior were investigated. The first class, 1,1-dichloro-2,2-(4-hydroxyphenyl)ethylidene (bisphenol C) based polymers, were found to be among the most fire-resistant polymers with peak heat release capacities as low as 20 J/g-K. Polymers containing bisphenol C all exhibited exothermic decomposition behavior. When compared to corresponding bisphenol-A-based polymers, these bisphenol-C-containing polymers had higher char yields and lower decomposition temperatures. The presence of bisphenol C in materials, whether as a co-monomer or blends, showed a char enhancement effect; yielding higher char than what is expected by a purely additive effect.

Bisphenol C polyarylates and polycarbonates yielded large amounts of HCl and carbon dioxide upon decomposition. Compared with other bisphenol-based polymers, polycarbonates and polyarylates containing bisphenol C yielded significantly less

amounts of monomer. Decreasing the concentration of bisphenol C in the copolymers or blends yielded relatively more monomer in the degradation products.

The second class of polymers studied were polycarbodiimides, which generally decompose in an endothermic manner to yield quantitative amounts of monomer. The incorporation of TEMPO-containing side-chain substituents altered the degradation. TEMPO-based polycarbodiimides decomposed in an exothermic fashion and yielded several other degradation products in addition to the original monomer. These free-radical-containing polymers showed a 25 % reduction in the peak heat release capacity when compared with the control polymer. Neither polymer was found to be fire resistant which is due to their high organic content and essentially 100 % weight loss during decomposition.

ABSTRACT

CORRELATING POLYMER FLAMMABILITY USING MEASURED PYROLYSIS KINETICS

MAY 1999

TALINE INGUILIZIAN, B. S., MASSACHUSETTS INSTITUTE OF TECHNOLOGY

M. S.Ch.E., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor Phillip R. Westmoreland

Polymer flammability was correlated using both new data and mechanistic pyrolysis models for standard and new polymers, including polycarbodiimides, polysiloxanes and polyhydroxyamides, which were designed to be flame-resistant. A new hybrid TGA/DSC/GC-MS apparatus was set up to perform thermal and mechanistic analysis on milligram-scale polymers and to determine properties that correlate with flammability data. A key characteristic parameter is maximum decomposition rate which, when coupled to the identity and the relative abundance of off-gases, measures the release rate of combustibles' chemical energy. The GC/MS identity of the decomposition gases also indicates the mechanistic pathways and the presence or absence of toxic fumes. In addition, a microscale combustion calorimeter similar the one developed at the FAA was built for comparison, providing continuous measurement of chemical heat release during combustion. The two apparata give complementary information on the

behavior of polymers in fire situations. Heat release rates from the two apparata were shown to correlate with each other and with large-scale, cone-calorimeter flammability tests.

The GC/MS data gave insight into the polymer decomposition mechanisms. In the cases of PMMA and poly(α-methylstyrene), the polymer depolymerized back to the monomer with negligble amounts of other products, apparently by bond fission and β-scission. The GC/MS also showed presence of co-monomers like butylmethacrylate in the case of PMMA. The products of polycarbodiimides implied a more complex decomposition, possibly involving concerted reactions and bond fission, that led to the formation of monomer and other products. Finally, the polysiloxanes' decomposition appeared to be quite complex. Both aromatic and non-aromatic siloxanes were produced with significant rearrangements of C-O and Si-O bonds. Mechanisms were suggested involving rearrangements by concerted reactions.

ABSTRACT

COMPUTATIONAL QUANTUM CHEMISTRY APPLIED TO NO_X CHEMISTRY AND NEW FIRE-RESISTANT POLYMERS

FEBRUARY 1999

KARIN ROTEM

B.S., LEHIGH UNIVERSITY

Ph.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Phillip R. Westmoreland

Computational quantum chemistry was used as a tool to predict needed thermochemistry and kinetics for two classes of problems: formation and destruction of NO_x pollutants and development of new fire-resistant polymers. Of the latter, polycarbodiimides and polyhydroxyamides (PHA's) were studied. Different methods were used: HF/6-31G(d), BAC-MP4 (bond-additivity corrections to UMP4 energies and HF vibrational frequencies), PM3 semi-empirical, and combinations.

On the NO_X problem, work focused on using theory to generate improved kinetics in $H_2/O_2/NO_X$ combustion. The results were a set of thermochemical data and high-pressure-limit kinetics for NO_X formation and destruction. Hartree-Fock structures and frequencies and fourth-order Moeller-Plesset energies were used for reactions of H/N/O-species involving $H_1N_1O_1$, N_1O_2, N_2O_1, $H_1N_2O_1$, and N_2O_2 surfaces, including $NH + NO \leftrightarrow N_2O + H$, $N_2O + O \leftrightarrow NO + NO$, $N + OH \leftrightarrow NO + H$, $N + O_2 \leftrightarrow NO + O$, and $N + NO \leftrightarrow N_2 + O$. Thermochemical results were discussed in the form of potential energy

surfaces. In general, BAC-MP4 heats of formation compared consistently well to literature data. The results generated from this work allowed evaluation of pressure-dependent kinetics and, ultimately, a refined group of reactions for the NO_x mechanism.

Strengths of particular bonds and bonding combinations in polycarbodiimides were calculated. Work focused on effects of R groups, chain size and stereoregularity on bond dissociation energies (BDE). Specifically, five polycarbodiimide systems were studied: (1) R=R′=H, (2) R=R′=CH_3, (3) R=R′=CH_2CH_3, (4) R=CH(CH_3)(phenyl), R′=H, and (5) R=CH(CH_3)(phenyl), R′=CH_3. Methyl- and ethyl-substituted polycarbodiimides decreased the bond strength of the central C-N bond. Ligands on the amine (backbone) nitrogen weakened its chain C-N bond dramatically. However, a lower barrier reaction has also been identified. Results imply rapid, concerted unzipping of this polymer, a result consistent with experiment.

For the polyhydroxyamide (PHA) system, a model cyclization reaction of PHA to polybenzoxazole (PBO) was evaluated. PHA cyclization to PBO has been studied experimentally, but a detailed theoretical reaction surface has never been evaluated. Moreover, a plausible mechanism by which PHA arrives at PBO had not been previously determined. The calculated overall heat of reaction was thermoneutral, and decomposition was determined to occur at 212°C, compared to the 215°C experimental value. The hydrogen-transfer reaction and a four-center concerted transition-state reaction were found to be the limiting steps.

ABSTRACT

POLYMER SURFACE MODIFICATION: CHEMICAL SURFACE MODIFICATION, LAYER-BY-LAYER ADSORPTION, AND SURFACE RECONSTRUCTION

SEPTEMBER 1997

WEI CHEN, B.A., SMITH COLLEGE

M.S., YALE UNIVERSITY

Ph.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor Thomas J. McCarthy

The three projects, chemical modification (Chapter 1), layer-by-layer deposition (Chapter 2), and surface reconstruction (Chapter 3),.that constitute this Ph.D. thesis are closely related in their overall objectives: using polymer surface modification to manipulate microscopic surface structures and control macroscopic properties.

Alcohol functionality can be introduced to the surface of poly(ethylene terephthalate) (PET) using either reduction or glycolysis; both of which cleave the PET chain. Both of these modified surfaces (PET-OH^R and PET-OH^G) and hydrolyzed PET (PET-OH/COOH) can be prepared using conditions that optimize surface functional group concentration, but minimize sample degradation. The surface alcohol density is higher on PET-OH^G than on PET-OH^R by a factor of ~2. The concentration of alcohols on reduced surfaces is increased by solvent annealing of the PET film prior to reduction. Reactivities of PET-OH^R and PET-OH^G samples were assessed and compared.

Layer-by-layer deposition of polyelectrolytes (poly(allylamine hydrochloride) and poly(sodium styrenesulfonate)) has been used to build up multilayer films on three organic polymer substrates: PET, PET-CO_2^- and PET-NH_3^+. XPS and contact angle data indicate that the layers are stratified and the wettability of the multilayer

assemblies is largely controlled by the identity of the outermost polyelectrolyte layer. The layer thickness and the stoichiometry of the deposition process (ammonium ion:sulfonate ion ratio) are affected by the substrate surface chemistry and can be controlled by adjusting the ionic strength of the polyelectrolyte solutions. Peel tests indicate that the multilayer assemblies show good mechanical integrity.

A perfluorohexylated-C_{60} (fullerene) was prepared and its surface activity and mobility were studied as a function of bulk concentration, annealing temperature, and annealing time in a polymer matrix (polystyrene). Perfluorohexylated-C_{60} is extremely surface-active in the polystyrene matrix and occupies 95% - 85% of the outermost 10 Å - 40 Å (XPS results), and renders a surface that is similar to a monolayer containing -CF_3 groups (hexadecane contact angle data). Surface reconstruction studies were carried out via either spin-casting or transferring a free standing polystyrene film over the composite materials (the surface-active agent and polystyrene). Both approaches show similar behavior of migration of perfluorohexylated-C_{60} from the bulk to the surface.

PUBLICATIONS

"Characterization of Two Precursor Polyblends: Polyhydroxyamide and Poly(amic acid)", *Polym. Eng. Sci.* **40**, 320 (2000), R.J. Farris and J.-H. Chang.

"Evaluation of Short Term – High Intensity Thermal Degradation of Graphite Fiber Reinforced Laminates via Ultrasonic Spectroscopy", *J. Polym. Sci., Part B: Poly. Phys.* **37**, 2601-2610 (1999), G. Schueneman, A.J. Lesser, T. Hobbs and B.M. Novak.

"Adsorption/Migration of a Perfluorohexylated Fullerene from the Bulk to the Polymer/Air Surface", *Macromolecules* **32**, 2342 (1999), T.J. McCarthy and W. Chen.

"Vinyl-Substituted Silphenylene Siloxane Copolymers: Novel High-Temperature Elastomers", *Macromolecules* **32**, 3426-3431 (1999), U. Lauter, S.W. Kantor, K. Schmidt-Rohr and W.J. MacKnight

"Thermal and Mechanical Properties of the Precursor Polymers: Comparison of Their Properties with Poly(amic acid)", *Polym. Eng. Sci.* **39**, 638 (1999), R.J. Farris and J.-H. Chang.

"Metal – Polymer Composites in Supercritical Fluid Carbon Dioxide", *Poly. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **40(1)**, 228 (1999), T.J McCarthy and P. Rajagopalan.

"Evaluation of Thermal Degradation of the Resin-Fiber Interface in Graphite Fiber Reinforced Laminates Using Ultrasonic Spectroscopy", *43rd SAMPE International Conference* **1**, 1042-1052 (1998), A.J. Lesser, G. Schueneman and T. Hobbs.

"Flame Retarding Properties of Phosphorus Containing Poly(amic acid)", *Korea Polym. J.* 6, **84** (1998), R.J. Farris, H.-J. Kim, J.-K. Choi, B.-W. Jo and J.-H. Chang.

"Thermally Stable Silphenylene Vinyl Siloxane Elastomers and Their Blends", *Macromolecules* **31**, 850 (1998), H.D. Zhu, S.W. Kantor and W.J. MacKnight.

"Effect of Heat Treatment on the Thermal and Mechanical Properties of a Precursor Polymer: Polyhydroxyamine", *Polymer* **39**, 5649 (1998), R.J. Farris, J.-H. Change, B.-W. Jo and M.J. Chen.

"Effect of TEMPO Stable Free Radicals on the Reduction of Polymer Flammability", *Polym. Prepr.* **39**, 653 (1998), R.J. Farris, J.R. Stewart and B.M. Novak.

"Synthesis and Characterization of Latent Fire Retardant Polymers: New TEMPO Substituted Polycarbodiimides", *Proc. of ACS, PMSE Div.* **78**, 31 (1998), R.J. Farris, J.R. Stewart and B.M. Novak.

"Adsorption/Migration of Surface – Active Fullerenes from the Bulk to the Polymer – Air Interface", *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **38(2)**, 676 (1997), T.J. McCarthy and W. Chen.

"Synthesis of Precursor Flame Suppressing Polymers," *Proc. 54th Annual Technical Conference, USA Soc. of Plastics Engineers, Indianapolis, IN.* 3072 (1996), C. Gao and S.W. Kantor.

UNIVERSITY SCIENTIFIC COLLABORATORS

FACULTY

Richard J. Farris (Principal Investigator)
Simon W. Kantor
Alan J. Lesser
William J. MacKnight
Thomas J. McCarthy
Bruce M. Novak
Philip R. Westmoreland

POST-DOCTORAL FELLOWS

Doohyun Baik
Wei Chen
Chunping Gao
Jungsoo Kim
David Long
Sueng Koo Park
Padma Rajagopalan
Stanislav Stoliarov

GRADUATE STUDENTS

Terry Hobbs
Taline Inguilizian
Haeyoung Kim
Greg Schueneman
Jennifer Stewart
Huiqing Zhang

UNDERGRADUATE STUDENTS

Jessie Ip

INDUSTRIAL COLLABORATORS
CUMIRP CLUSTER F

The FAA funded program at the University of Massachusetts Amherst entitled, "High Performance Fire-Safe Polymeric Materials" was incorporated into the Center for UMass / Industry Research Polymers (CUMIRP). This Center provided a forum that allowed industry to participate in the research program. A primary objective of the Center program is to promote the effective translation of the research performed at the University into viable technology for industrial commercialization. In addition to the Federal Aviation Administration, 15 companies and government agencies participated interactively in the program. The complete list of Cluster F participants is noted below.

1995 – 1999 MEMBERS LIST

Akzo

BP / Amoco Plastics, Inc.

Boeing – Commercial Airplane Group

Ciba Specialty Chemicals

DuPont – Advanced Fibers Systems

Federal Aviation Administration

General Electric Co. / GE Plastics

GP Resins

Monsanto Chemical Co.

National Science Foundation (through I / UCRC program)

Old Deerfield Fabrics, Inc.

Schneller, Inc.

Solutia, Inc.

Titeflex

UCAR Carbon

U.S. Army