FURTHER CALORIMETRIC EVALUATION OF POLYMER/OLIGOMER DECOMPOSITION: APTAC TESTING

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ABSTRACT

The behavior of polymers and oligomers subjected to elevated temperatures in an air-free environment was recently studied to characterize the energetics of polymer/oligomer decomposition. This work, which focused exclusively on hydrocarbon and oxygenated species tested in an open-pan DSC/TBA, was pursued to test a widely-held notion that polymer decomposition is endothermic in nature. Selected species have now been tested in the APTAC, a calorimeter designed to provide an adiabatic environment for runaway reaction characterization. Comparison of results with those from the DSC/TGA reveals confirmation of energetics in some cases and startling differences in others. For example, in both the DSC/TGA and the APTAC, polymers with double bond or glycidyl groups display exothermic reactions. However, polymers with ether or ester functionalities can exhibit exothermic decomposition behavior in the APTAC—in contrast to the DSC/TGA results. These findings reinforce the hypothesis that loss of heat by vaporization and removal of reactive intermediates by carrier gas in the DSC/TGA can confound the observed energetics of polymer/oligomer reaction. Furthermore, functional groups present in polymers/oligomers can strongly influence the reaction energetics.

INTRODUCTION

Numerous studies have been performed to analyze polymer degradation through, for example, kinetics measurement and off-gas composition, from the perspective of product quality and performance [1-6]. The understanding that is obtained can enable improvement in polymer design and application. These studies, however, provide only part of the information needed to examine the potential for temperature and/or pressure excursions in the event the material is deliberately or inadvertently subjected to excessive temperatures.   Such process safety considerations are relevant to the manufacture and industrial use of these materials.

An investigation was recently conducted to characterize the energetics of reaction of various types of polymers and oligomers at elevated temperature [7]. The motivation for this work was the widely-held notion that polymer decomposition must necessarily be endothermic if the polymer itself is made via an exothermic process. Since decomposition products are not necessarily the same as the constituent monomers, this notion is not necessarily true. In fact, in work carried out in a DSC/TGA (to allow simultaneous indication of heat generation/absorption and weight loss) with flowing nitrogen (an air-free environment), several polymers types were found to react exothermically. Even in the midst of this study, comparison of the open-system results with prior piecemeal experience from closed systems hinted that some oligomers/polymers undergoing endothermic reaction in the DSC might behave otherwise in a closed, adiabatic environment.

To understand more clearly the energetic behavior at elevated temperatures, testing of a limited number of oligomers/polymers has been carried out in the APTAC, an adiabatic calorimeter available from Arthur D. Little, Inc. Results from these tests demonstrate that a wide variety of species do undergo exothermic reaction when heated to moderate temperatures and that substantially different behavior can be observed between closed and open systems.

EXPERIMENTAL

Equipment
DSC/TGA: Previous testing of decomposition energetics [7] involved screening of samples via open-pan differential scanning calorimetry (DSC) in combination with thermal gravimetric analysis (TGA). These tests were performed in a Netzsch STA 409 simultaneous DSC/TGA instrument. Aluminum sample pans were employed, holding 5-20 mg of sample. Nitrogen purge gas flowed across the sample pans at a 50 cc/min rate. Heat rates were 5°C/min from room temperature up to a maximum temperature of 450°C.

Adiabatic Calorimetry: Testing for the current study was carried out in the Automatic Pressure Tracking Adiabatic Calorimeter (APTAC) available from Arthur D. Little, Inc. The internals of this calorimeter are depicted in Figure 1. The operating principle of this calorimeter is to provide an environment surrounding the sample bomb that minimizes the heat loss from the sample and sample bomb. This allows the sample undergoing an exothermic reaction to self-heat at a rate and extent comparable to that in a large-scale, adiabatic environment. This is accomplished by placing the sample bomb in a containment vessel (Parr vessel) and heating the gas space surrounding the bomb to match the internal temperature of the bomb. Thermocouples are placed inside the sample bomb and gas space of the containment vessel for this purpose.

A thin-wall sample (0.020 in titanium) bomb is employed to reduce the thermal capacitance of the bomb and, thereby, limit the amount of heat absorbed by the sample bomb from the sample. While this spherical bomb can normally withstand pressure differentials of up to 400 psi, the instrument also adjusts the pressure in the containment vessel to match the pressure in the bomb (transducers are supplied for this purpose). In this set-up, sample pressures reaching nearly 2000 psia can be accommodated.

Stirring is accomplished via magnetic coupling between a magnet-equipped drive within the containment vessel and a ¾" length teflon-coated magnetic stir bar inserted into the sample bomb. Three-zone heating is provided in the containment vessel along with an additional heater for the tubing bundle connected to the sample bomb. The APTAC can match temperature and pressure rise rates of up to 400°C/min and 10,000 psi/min, respectively. Since the instrument currently does not have cooling capability, its lower temperature limit of operation is room temperature and it is incapable of tracking endothermic reactions or processes. The calorimeter can tolerate temperatures in excess of 450°C for brief periods.

The APTAC is typically operated in the heat-wait-search mode. That is, the sample is heated to a pre-selected temperature and upon reaching this temperature, the instrument waits for a period of time (usually 25 minutes) for the bomb and containment vessel temperatures to stabilize. After the wait period, the instrument continues at that temperature (for another 25 minutes) to determine if there is any exothermic activity. During this time, the temperature of the containment vessel gas space is adjusted to match that of the sample thermocouple. If no heat-up activity exceeding a pre-set exotherm threshold is observed, it is concluded that there is no exotherm. The sample is then heated to the next temperature and the process repeated. If an exotherm is detected, the APTAC tracks the sample conditions and adjusts the temperature and pressure of the containment vessel accordingly (adiabatic or exotherm mode).

The quoted detection limit of the APTAC is 0.04°C/min (comparable to the 0.02°C/min value of the Accelerating Rate Calorimeter). In this study, onset temperatures of 0.06-0.08°C/min were employed to reduce the likelihood of the occurrence of "drift", in which a slight thermocouple calibration imbalance yields a slow temperature rise rate and is interpreted as an exotherm.

The APTAC containment vessel is rated for 2500 psig and is designed to withstand rupture of the sample bomb (as long as the sample is not an explosive-grade material). To protect the instrument from possible damage, tests will shutdown under certain conditions. The shutdowns employed in this study include:

high temperature	= 500ºC	high pressure	= 1600-1800 psia (per gas supply)
high self-heat rate	= 2000ºC/min	high pressurization rate	= 10,000 psi/min

In addition, tests were terminated if no exotherms were detected by 380-390ºC (on-going exotherms were allowed to continue, though, until the reactions stopped or a shutdown condition was reached).

Samples
Testing of species in the APTAC requires more instrument material, time and labor costs than would be incurred in a standard DSC or DSC/TGA. A limited number oligomers and polymers were therefore selected from the classes of hydrocarbons and oxygenates explored previously

➢ Polypropylene   (class: polyolefins) – Aldrich #42,811-6, MW~12,000
➢ Polybutadiene   (class: polydiolefins) – Aldrich #43,477-9, MW~1,800
➢ Polystyrene   (class: polystyrene) – Aldrich #43,010-2, MW~230,000
➢ Polyethylene glycol   (class: polyethylene glycols) – Aldrich #20,244-4,M_n~3,400
➢ Polypropylene glycol   (class: polypropylene glycols) – Aldrich #20,235-5),M_n~4000
➢ EPON HPT® Resin 1050   (class: glycidyl ethers) – Shell Chemical Company
➢ Polyvinylmethyl ketone   (class: polyketones) – Aldrich #18,274-5, MW~500,000
➢ Polyvinylphenyl ketone   (class: polyketones) – Aldrich #43,428-5
➢ Polyacrylic acid   (class: polyacids) – Aldrich #30,620-7, M_v~750,000
➢ Polyethylene terephthalate   (class: polyesters) – Aldrich #20,025-5, M_v~18,000
➢ Polybisphenol acetone carbonate (class: polycarbonates) – Aldrich #18,164-1,MW~29,000

As before, no attempt has been made to identify or to assess impact of additive packages that may be contained within the materials tested.

Procedures
Titanium sample bombs were rinsed with acetone and dried prior to use. Samples of 25-40 gram quantity were placed in the titanium bomb with air exposure. A teflon-coated, magnetic stir bar was also added. Typically, the weight of the bomb and stir bar was about 38 grams. Once mounted on the calorimeter, the bomb was evacuated with a rotary vane mechanical pump to under 2 psia and re-pressured with cylinder nitrogen to 20-30 psia. The evacuation/re-pressurization steps were repeated four more times.

Samples were initially heated to a temperature between 75 and 200ºC (depending on the sample type). Heat-wait-search steps commenced immediately thereafter. Stirring rates were typically 200 rpm.

RESULTS AND DISCUSSION

Calorimetric Characterization
APTAC results for this study are summarized by plots of self-heat and pressurization rates versus time and pressure versus temperature. The APTAC self-heat rate should relate to the heat flow of a DSC. For the closed environment of the APTAC sample bomb, the pressure corresponds to the weight loss of the sample in the open pan TGA. The pressurization rate would reflect the rate of weight loss in the TGA.

Due to the accelerating nature of exothermic reactions in adiabatic conditions, self-heat and pressurization data are often plotted in logarithmic plots. Inspection of the self-heat rate as a function of reciprocal temperature reveals that such a plot is, in fact, akin to an Arrhenius plot and the slope is related to the activation energy [8]. Likewise, kinetic information is contained in the pressurization rate data (provided the composition of the gas/vapor species is understood). In this manner, calorimetric data from dynamic, adiabatic experiments can be employed to extract lumped reaction kinetics, although this type of analysis is not pursued in the present study.

Polypropylene
The APTAC results for the 12,000 MW polypropylene are shown in Figures 2a and 2b. One of the most noticeable features of Figure 2a is the appearance of "humps" between 160 and 280ºC in both the self-heat and pressurization curves. These "humps" reflect the heat-wait-search steps the instrument is conducting as it searches in this temperature range for an exotherm.

As expected for this material, no exothermic activity is observed for temperatures up to 385ºC (the point at which the calorimeter had been instructed to terminate the experiment). Two regions of "drift" occur in the 270-280ºC and 310-340ºC range. However, beyond about 340ºC, the pressurization rate is seen to accelerate and reaches a level of about 3½ psi/min at 385ºC. This behavior indicates the temperature range in which decomposition is initiating.

By comparison, the DSC/TGA results for this material, found in Figure 2c, showed an onset temperature of 390ºC for endothermic activity and weight-loss. The distinctive 140-170ºC melt endotherm in the DSC trace is not detected in the APTAC on account of the inability of the APTAC to respond directly to endotherms.

Polybutadiene
Exothermic activity for the polybutadiene sample (MW=1,800) is found to initiate in the APTAC at about 245ºC (Figure 3a). (In actuality, the exotherm just missed detection at the earlier heat-wait-search step at 221ºC. The extrapolated slope of the self-heat rate curve to lower temperatures lines up with the measured heat generation rates and reflects actual "detection" of the exotherm at temperatures as low as 200ºC.) This exotherm continued until the temperature reached above 500ºC. Accompanying the exotherm are two distinct regions of pressurization behavior. A slow increase in pressurization rate is exhibited in the region between 245 and 385ºC, yielding an overall pressure increase of 27 psi. This region can be attributed to saturation of existing double-bonds, such as might occur in cross-linking. Above 385ºC, the pressurization rate jumps to over 2000 psi/min and ultimately generates a pressure of over 1600 psia in the sample bomb (Figure 3b). The behavior in this region reflects actual decomposition of material.

In the DSC/TGA results for this same sample (Figure 3c), a significant exotherm occurs between 270 and 420ºC and is coupled with a modest loss of weight. Beyond 420ºC, an endotherm develops along with more extensive weight loss. These findings are qualitatively consistent with the behavior found in the APTAC.

Polystyrene
Adiabatic testing of the polystyrene sample (MW ~ 270,000) shows onset of exothermic activity in the vicinity of 180ºC (Figure 4a). The modest exotherm seen for this sample reaches a maximum self-heat rate of 0.5ºC/min and is accompanied by a maximum pressurization rate of 3.5 psi/min. The rates observed in this test, though, occurred alongside poor heater control after reaching 280ºC. Significant decomposition appears to take place after 350ºC as evidenced by the upturn in pressure in the pressure vs. temperature plot (Figure 4b). It can be inferred that much of the 700 psia pressure developed in the course of the experiment is comprised of condensible vapor species since the pressure returns to under 60 psia by the time the sample has cooled to 50ºC.

An exotherm is displayed in Figure 4c at about 240ºC in the DSC trace for the same material. This is followed by a substantial endotherm and weight loss at 410ºC. This polystyrene sample was actually not one of the ones tested in the previous DSC/TGA paper. To provide a sufficient quantity for APTAC testing, it was necessary to procure a different polystyrene sample. Curiously, none of the previous seven polystyrene samples exhibited significant exothermic activity, yet the current sample does. Apparently, residual styrenic double bonds must still be present in this sample.

Polyethylene glycol
The polyethylene glycol sample (M_n = 3,400) exhibits an exotherm in the APTAC (Figure 5a) beginning at 280ºC and accelerating up to several hundred degrees C per minute through the end of the test (above 500ºC). The pressure rise rate increases to about 4500 psi/min, turns negative between 455 and 500ºC (thus, it does not show up on a log-log scale) and then returns to about 1300 psi/min until the end of the test. It is not clear whether this change in pressure rate direction is due to possible plugging of the sample transducer line or to consumption of vapor-phase species. A pressure of nearly 1900 psia develops by the end of the exotherm (Figure 5b).

Surprisingly, no indication of a significant exotherm is found in the corresponding DSC data (Figure 5c). An *endotherm* and sharp loss of mass is observed above 350ºC. In this case, it appears that the TGA and APTAC pressurization data agree, but with substantially different results on the energetics.

Polypropylene glycol
The same qualitative behavior of the polyethylene glycol is observed in Figure 6a for the polypropylene (M_n = 4,000) sample. A modest exothermic is found in the APTAC at 325ºC (and it may be argued that it actually begins closer to 300ºC) and continues to 370ºC (at which point, system pressure caused the test to end). The peak self-heat rate is only 1.7ºC/min, compared with over 500ºC/min for polyethylene glycol. Pressurization initiates between 300 and 325 and also continues as long as the temperature increases (Figure 6b).

In contrast, Figure 6c shows the DSC results for this sample in which an *endotherm* begins in the same 300-325ºC temperature range along with a substantial weight loss. Once again, the APTAC yields energetics that are contrary to those found in the DSC.

Polyglycidyl ether
The phenolic-based glycidyl ether of Shell Chemical, EPON HPT® Resin 1050, displays self-heating and pressure rise initiating at about 250ºC (Figure 7a). These rates accelerate to levels approaching 4,000ºC/min and 62,000 psi/min, respectively, by the time 500ºC is reached. Up to 420ºC, a total sample pressure of only 360 psia develops (Figure 7b); thereafter, the pressure

quickly rises to over 2000 psia and results in sample bomb rupture as the system was unable to match the high pressurization rate.

Exothermic activity and *moderate* weight loss occur, starting at 260-300ºC, for the same sample in the DSC/TGA results of Figure 7c. However, the exothermic behavior ceases in the DSC after about 410ºC while continuing to 500ºC in the APTAC.

Polyketones

Two polyketones, polyvinylmethyl ketone and polyvinylphenyl ketone were tested in the APTAC. The ketone groups in both of these polyketones are attached to, but do not comprise part of the essentially poly-ethylene backbone. The polyvinyl methyl ketone results appear in Figure 8a. Two exothermic peaks are observed, initiating at 122ºC, reaching a local maximum at 162ºC, and then continuing through another maximum at about 205ºC. All exothermic activity disappears at about 260ºC. Pressurization of the system accompanies the self-heating, exhibiting two better-defined peaks, and also stopping around 260ºC. No further exothermic or pressure-building behavior is observed up to 390ºC—at which point, the experiment had been programmed to end. A pressure of over 1000 psia developed during the test, as seen in Figure 8b.

Two modest and well-separated exotherms were found in the DSC test of the sample (Figure 8c). Onset temperatures for these exotherms were 180ºC and 275ºC, respectively. Significant weight loss begins at the end of the first exotherm, continues during the second exotherm and becomes substantial above about 325ºC.

Results for the polyvinyl phenyl ketone are shown in Figure 9a. No significant exothermic activity is observed for this material--either a very minor exotherm or drift appears at temperatures above 280ºC. At this same temperature range, an increase in pressurization rate begins, generating several hundred psia pressure in the sample bomb. Above 350ºC, the sample pressure rapidly pressures to nearly 1000 psia (Figure 9b).

The DSC trace for this sample reveals a pronounced endotherm starting at 285ºC, reaching a peak at 370ºC, and continuing to 380ºC (Figure 9c). The TGA indicates weight loss beginning at about 300ºC and nearing completion when the endotherm is finished.

Polyacrylic acid

No exotherms are observed in the APTAC for the polyacrylic acid (M_v = 750,000) up to a temperature of 380ºC (Figure 10a). Pressurization appears to accelerate significantly around 260ºC toward a maximum pressurization rate of about 7 psi/min. Despite this modest pressurization rate, temperatures are maintained in this range sufficiently long for the sample bomb pressure to reach nearly 1200 psia (Figure 10b).

A series of endotherms are exhibited for the polyacrylic acid in the DSC (Figure 10c). The most prominent endotherm initiates at 120ºC and extends to 280ºC. This peak is accompanied by weight loss at about 200ºC that gradually accelerates with higher temperatures.

Polyethylene terephthalate

The APTAC self-heat rate plot (Figure 11a) for polyethylene terephthalate (M_v ~ 18,000) shows modest exothermic activity beginning around 140ºC and gradually accelerating with increasing temperature. This trend continued until 435ºC when a power interruption terminated the test prematurely (probably by no more than 4 minutes early). A significant pressure rise rate is seen to appear at 280ºC, rising rapidly to over 100 psi/min by the end of the experiment. By the end of the exotherm, the pressure climbed to over 900 psia (Figure 11b).

In contrast to the APTAC results, a well-defined *endotherm* between 230 and 265ºC appears in the DSC plot of Figure 11c. This peak is followed by another endotherm at 385ºC. No evidence of exothermic activity is displayed at elevated temperatures. Moreover, significant weight loss does not occur until about 380ºC.

Polycarbonate

A modest exotherm is observed in Figure 12a for a polybisphenol acetone carbonate sample tested in the APTAC. This exotherm initiates at about 160ºC and continues a slow rise in rate until the experiment terminates at 440ºC. A gradual increase in pressure with an upturn in pressurization rate at 380ºC accompanies this exotherm. The total pressure developed in the test (for the maximum 440ºC temperature reached) was only about 130 psia (Figure 12b). Most of this pressure rise is from temperature effect on the gas, although about 25 psia of non-condensible gas (as indicated at 50ºC) was evidently produced.

Essentially no significant thermal activity is found for this same material in the DSC/TGA (Figure 12c). Perhaps the APTAC has sufficient sensitivity to pick up modest exotherms that might otherwise be missed in the DSC. The minor degree of pressure build-up in the APTAC is consistent with the absence of substantial weight loss in the same temperature range for the TGA.

General Observations

It is obvious that broad conclusions cannot be drawn for a class of materials based on analysis of merely one sample of one type of oligomer or polymer. The tests that have been performed in this study, though, should provide a glimpse into the behavior of these compounds at moderately high temperatures. In particular, adiabatic testing has demonstrated that exothermic reactions may occur for oligomers/polymers containing double bond, ether, epoxy, carbonyl, ester, or carbonate functionality. Recognition that the products of polymer decomposition may differ from the constituent monomers leads to the consideration that the energetics of decomposition may be different than the reverse of polymerization.

The tests in the current study support the finding that reaction energetics in an adiabatic calorimeter may be different than those measured in an *open* DSC. DSC testing is clearly valuable for examining phase changes, volatility, and reactivity of samples. However, species that undergo thermal-neutral or endothermic reaction at elevated temperature in the open DSC may exhibit exothermic behavior in the APTAC. Two key differences in the sample environment contribute to this difference. Volatilization of light components into the carrier gas of an open pan system (1) takes substantial latent heat from the sample and (2) removes potential reactive intermediates. Testing in a *closed* DSC (e.g., samples contained in sealed glass capillaries) is expected to negate these effects. Use of hermetically-sealed DSC pans may not suffice on account of the inability to withstand the internal pressures that develop during such tests. For this reason, it is recommended that caution be exercised when choosing instruments and accessories to assess the potential for exothermic or pressure-generating reactions. Testing in a closed environment should provide more reliable reactivity results than in an open environment. Note that adiabatic calorimeters lacking cooling capability, though, cannot directly reveal and monitor endothermic reactions.

Comparison of the APTAC and DSC results reinforces the observation that onset temperatures for reactions are consistently lower in an adiabatic calorimeter than in the DSC. For the samples in this study, this difference amounts to 30-60ºC. The source of this difference is the high sensitivity toward exothermic reactions and the lack of temperature ramping in the adiabatic calorimeter. Thus, to gauge the temperature at which exothermic or pressure-generating reactions

may become noticeable, use of an adiabatic calorimeter is preferred. Moreover, application of good engineering practice, such as imposition of a safety margin between maximum operating and decomposition onset temperatures is recommended.

CONCLUSIONS

Testing of selected hydrocarbon and oxygenated-hydrocarbon oligomers/polymers in the closed, nitrogen-filled environment of the adiabatic APTAC calorimeter has revealed exothermic reaction in some of these materials. Specifically, compounds containing double bonds, ether linkages, epoxy groups, ketones, esters, or carbonate groups may impart exothermic behavior at elevated temperatures. In addition, such exothermicity may be masked in open-pan differential scanning calorimetry, presumably due to removal of latent heat and of reactive species in the open environment. Onset temperatures for reactions in the APTAC are found to be 30-60ºC lower than those observed in the DSC. For these reasons, closed-system calorimetry is recommended for assessing energetics of reactions; closed-system adiabatic calorimetry is preferred for evaluating the potential and kinetics of exothermic or pressure-generating reactions.

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TABLE: COMPARISON OF APTAC AND DSC/TGA RESULTS

Sample			DSC/TGA			APTAC							
ID	Class	Source	Type	T_{onset} [C]	Wt Loss [%]	Test ID	Type	T_{onset} [C]	T_{max} [C]	P_{max} [psia]	$dT/dt\|_{max}$ [C/min]	$dP/dt\|_{max}$ [psi/min]	Thermal Inertia[2], ϕ
Polypropylene MW~12,000	Polyolefin	Aldrich #42,811-6	a) Endo b) Endo	a) 125 b) 395	a) 0 b) 60+	A00140	-----	-----	-----	243	-----	3.4	1.19
Polybutadiene MW~1,800	Polydiolefin	Aldrich #43,477-9	a) Endo b) Exo c) Endo	a) 35 b) 270 c) 420	a) 0 b) 16 c) 32+	A00117	Exo	244	518	1627	887	2990	1.20
Polystyrene MW~230,000	Polyaromatic	Aldrich #43,010-2	a) Exo b) Endo	a) 244 b) 412	a+b) 100	A00201	Exo	182	436	702	0.49	3.5	1.20
Polyethylene glycol Mn~3,400	Polyethylene glycol	Aldrich #20,244-4	c) Endo d) Endo	c) 55 d) 350	a) 0 b) 100	A00112a	Exo	281	523	1870	527	4580	1.19
Polypropylene glycol Mn~4,000	Polypropylene glycol	Aldrich #20,235-5	a) Endo b) Endo	a) 35 b) 295	a) 0 b) 98	A00122	Exo	325	372	1780	1.7	71	1.20
EPON HPT® Resin 1050	Glycidyl ether	Shell Chemical	Exo	300	62	A00126	Exo	252	540	2050	4350	61700	1.19
Polyvinyl methyl ketone MW~500,000	Polyketone	Aldrich #18,274-5	a) Endo b) Exo c) Exo d) Exo	a) 45 b) 180 c) 275 d) 405	a) 0 b) 4 c) 65 d) 21+	A00193	a) Exo b) Exo	a) 122 b) 184	390	760	a) 0.17 b) 0.66	a) 0.69 b) 4.6	1.28
Polyvinyl phenyl ketone	Polyketone	Aldrich #43,428-5	a) Endo b) Endo	a) 55 b) 285	a) 0 b) 93	A00157	Endo	-----	-----	970	-----	2.1	1.20
Polyacrylic acid Mv~750,000	Polyacid	Aldrich #30,620-7	a) Endo b) Endo c) Endo	a) 40 b) 115 c) 300	a) 0 b) 19 c) 53+	A00147	Endo	-----	-----	1180	----	6.8	1.39
Polyethylene terepthalate Mv~18,000	Polyester	Aldrich #20,025-5	a) Exo b) Exo c) Endo d) Endo	a) 55 b) 120 c) 230 d) 385	a) 0 b) 0 c) 0 d) 80	A00199	Exo	142	441[1]	920[1]	9.9[1]	163[1]	1.24
Polybisphenol acetone carbonate, MW~29,000	Polycarbonate	Aldrich #18,164-1	No peaks	-----	-----	A00202	Exo	162	439	130	2.4	1.7	1.27

[1]Run terminated prematurely due to power interruption

[2]Ratio of total thermal capacitance to that of sample; heat capacity of sample assumed to be 0.5 cal/gC

FIGURE 1: AUTOMATIC PRESSURE TRACKING ADIABATIC CALORIMETER (APTAC)

Sample TC

Gas/Liquid Injection — P Transducer

Controlled Vent —

Nitrogen TC

Heaters

Reaction Vessel

Pressure & Temperature
Controlled Chamber

Pressure Vessel

Ceramic Insulation

Stirring Magnet
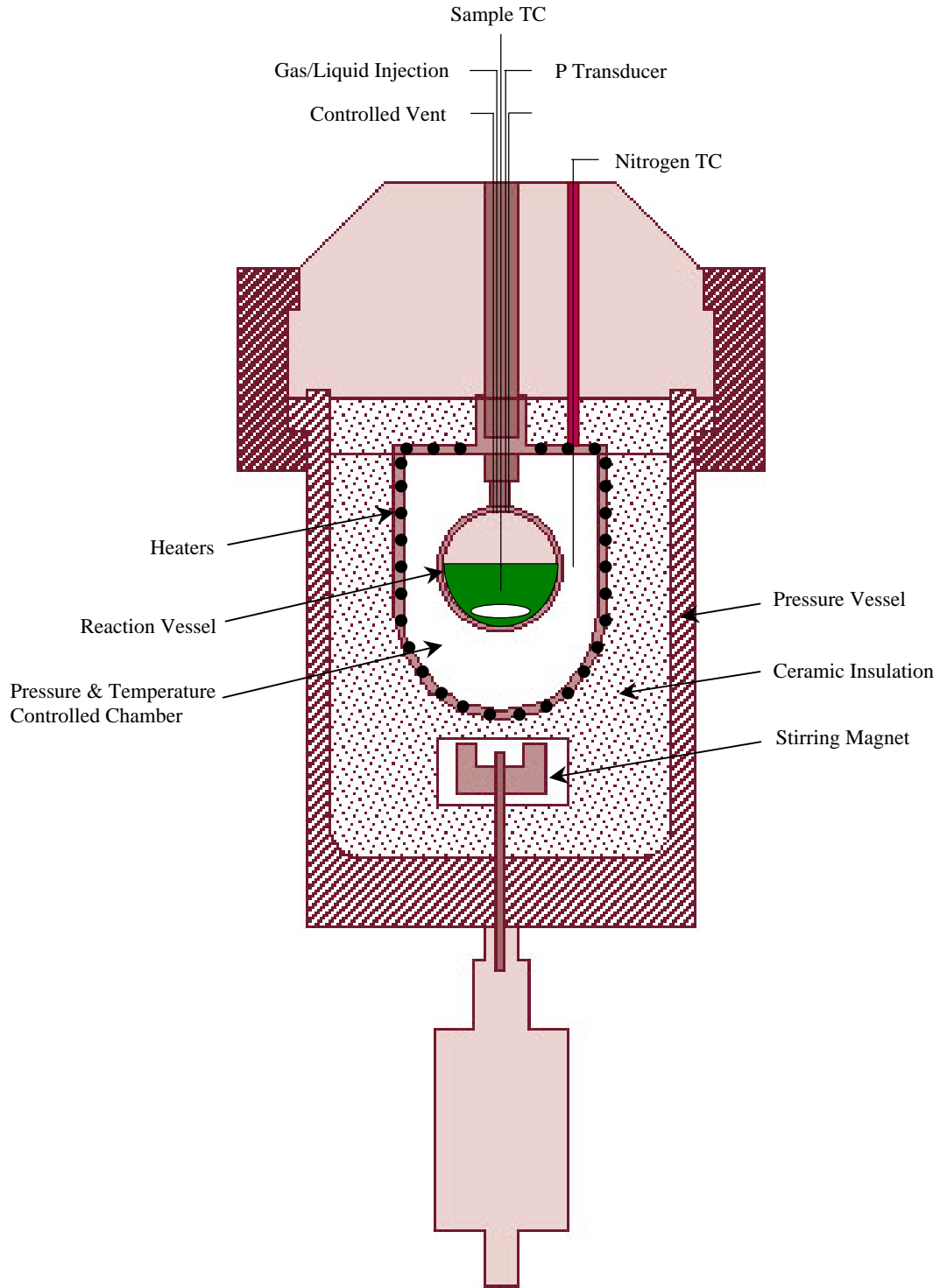
FIGURE 2a: CALORIMETRIC TESTING OF POLYPROPYLENE - T,P RATES
APTAC; Nitrogen

Legend:
- Self-Heat Rate - Polypropylene, MW=12,000 (A00140; APTAC)
- Pressurization Rate - Polypropylene, MW=12,000 (A00140; APTAC)

Y-axis: Self-Heat Rate [C/min] or Pressurization Rate [psi/min]
X-axis: Temperature [C]
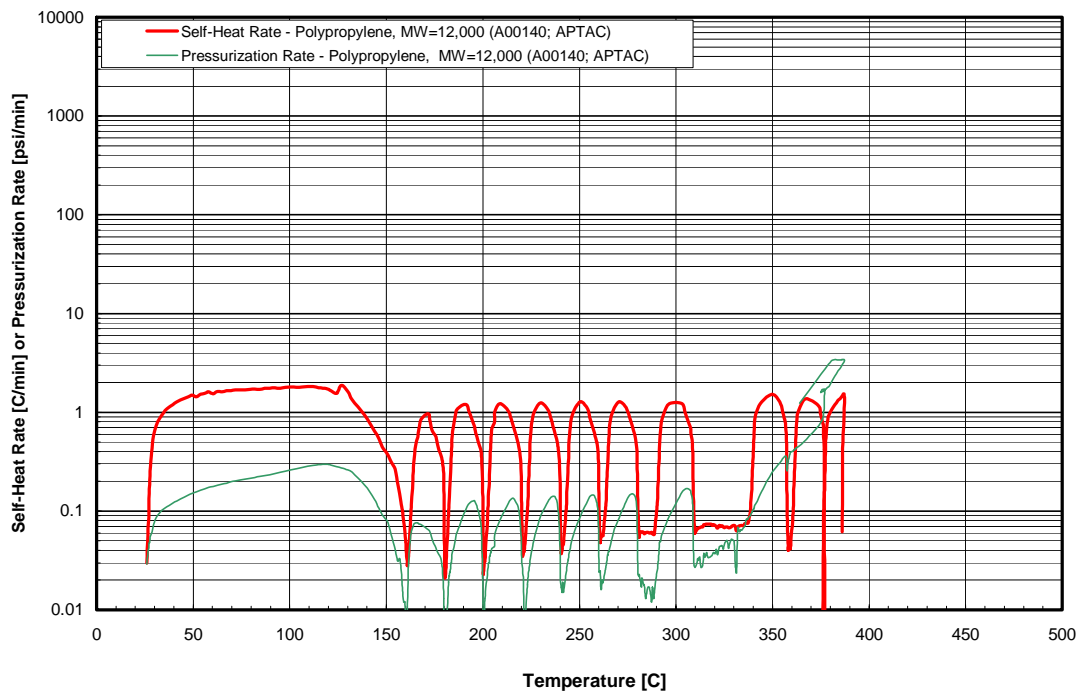
FIGURE 2b: CALORIMETRIC TESTING OF POLYPROPYLENE - P vs. T
APTAC; Nitrogen

Labels: Cooling, Heating

Y-axis: Pressure [psia]
X-axis: Temperature [C]
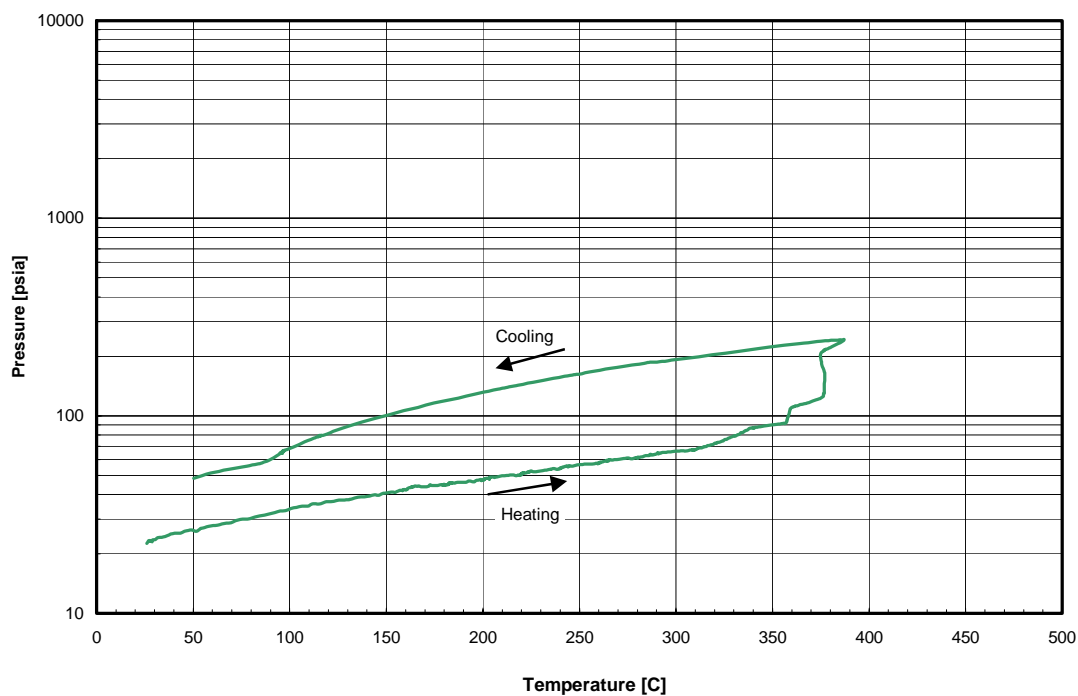
FIGURE 2c: CALORIMETRIC TESTING OF POLYPROPYLENE
Netzsch DSC/TGA; Flowing Nitrogen
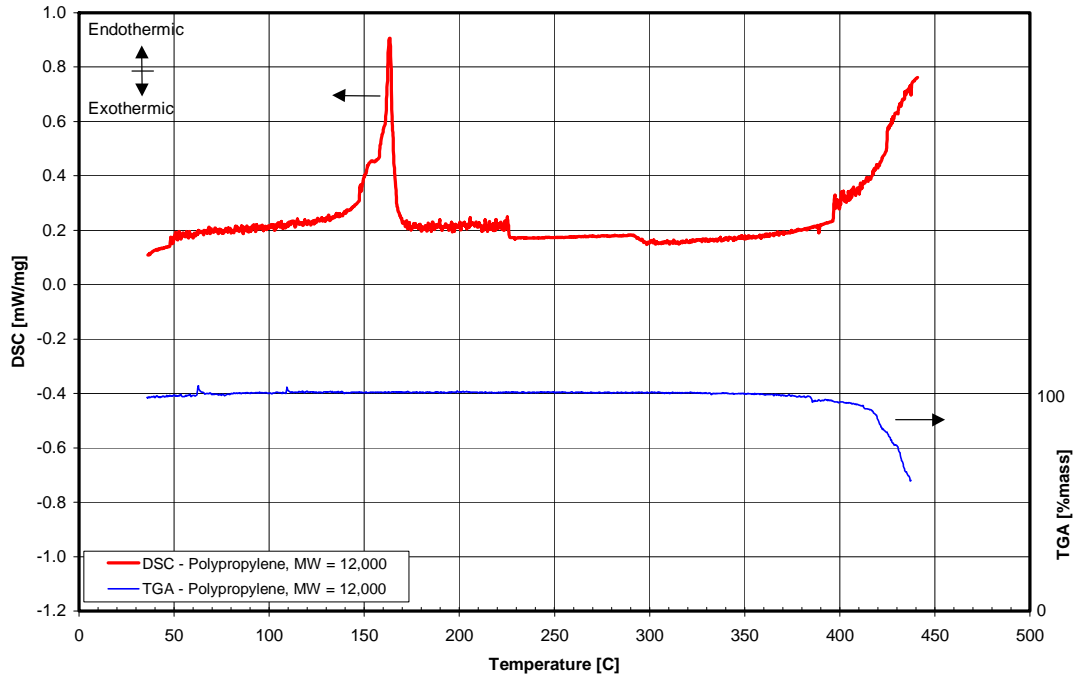
FIGURE 3a: CALORIMETRIC TESTING OF POLYBUTADIENE - T,P RATES
APTAC; Nitrogen
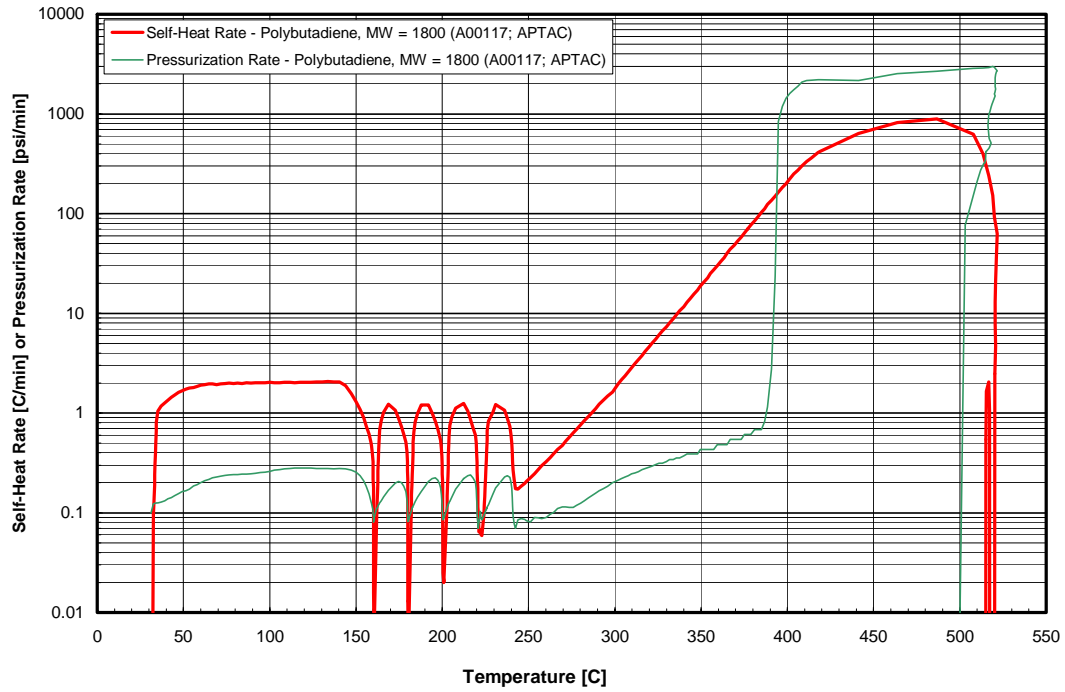
FIGURE 3b: CALORIMETRIC TESTING OF POLYBUTADIENE - P vs. T
APTAC; Nitrogen
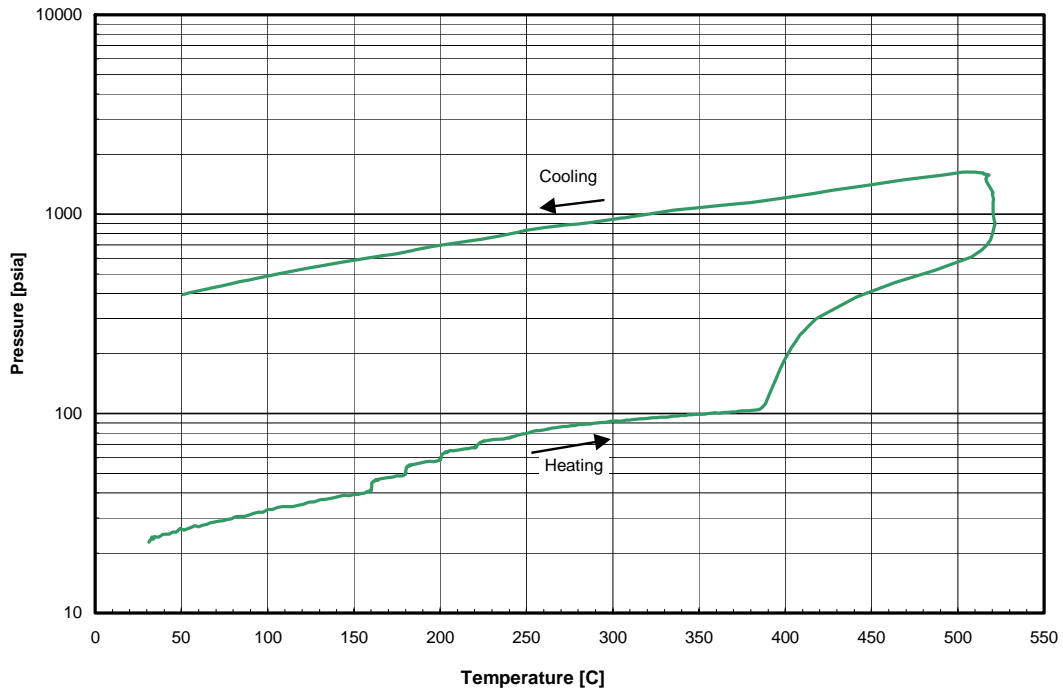
FIGURE 3c: CALORIMETRIC TESTING OF POLYBUTADIENE
Netzsch DSC/TGA; Flowing Nitrogen
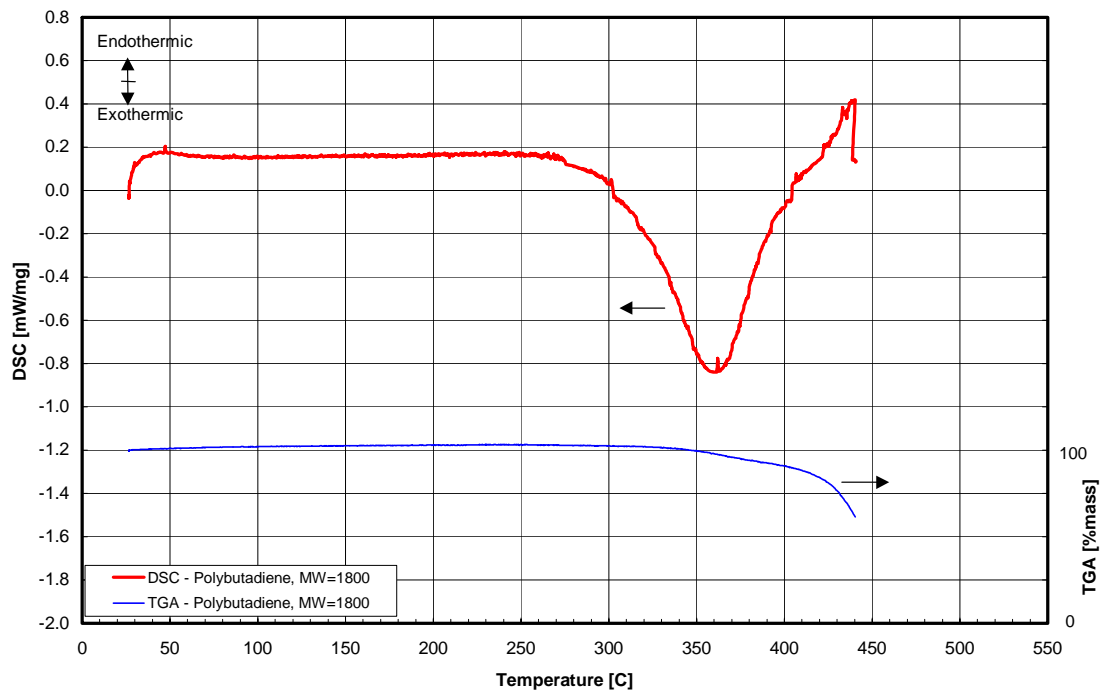
FIGURE 4a: CALORIMETRIC TESTING OF POLYSTYRENE - T,P RATES
APTAC; Nitrogen

Legend:
- Self-Heat Rate - Polystyrene, Mv=750M (A00202; APTAC)
- Pressurization Rate - Polystyrene, Mv=750M (A00202; APTAC)

Y-axis: Self-Heat Rate [C/min] or Pressurization Rate [psi/min]
X-axis: Temperature [C]

Annotation: Heater control problems
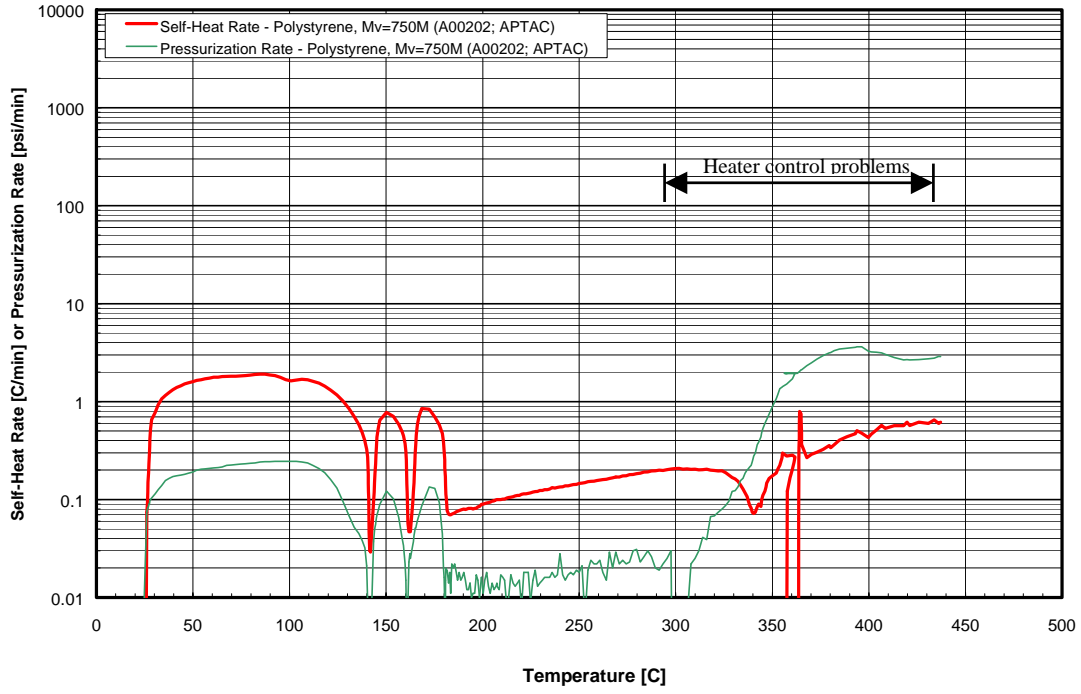
FIGURE 4b: CALORIMETRIC TESTING OF POLYSTYRENE - P vs. T
APTAC; Nitrogen

Y-axis: Pressure [psia]
X-axis: Temperature [C]

Annotations: Cooling, Heating
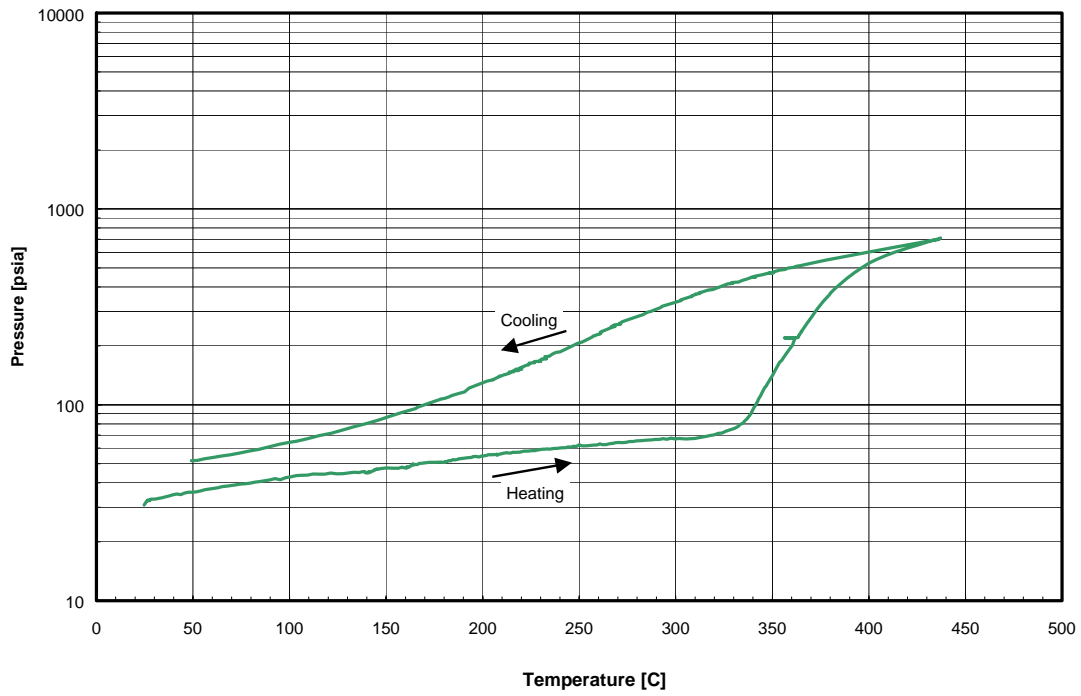
FIGURE 4c: CALORIMETRIC TESTING OF POLYSTYRENE
Netzsch DSC/TGA, Flowing Nitrogen

DSC - Polystyrene, MW = 230,000 (Aldrich #43,010-2)
TGA - Polystyrene, MW = 230,000 (Aldrich #43,010-2)
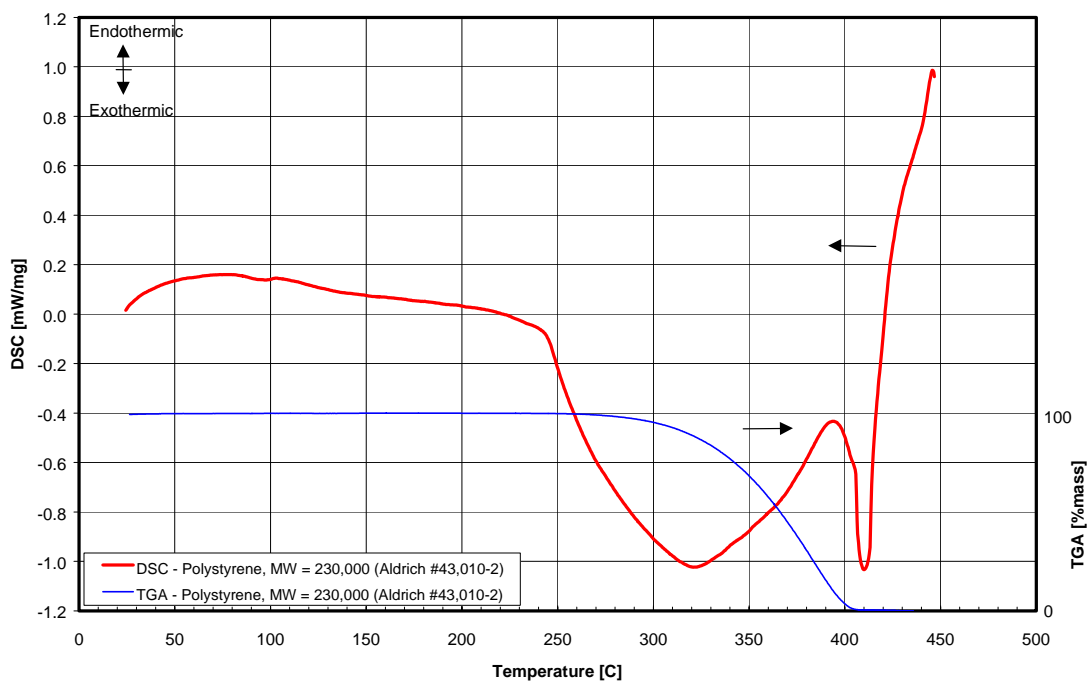
FIGURE 5a: CALORIMETRIC TESTING OF POLYETHYLENE GLYCOL - T,P RATES
APTAC; Nitrogen

Self-Heat Rate - Polyethylene Glycol, Mn=3,400 (A00112a; APTAC)
Pressurization Rate - Polyethylene Glycol, Mn=3,400 (A00112a; APTAC)
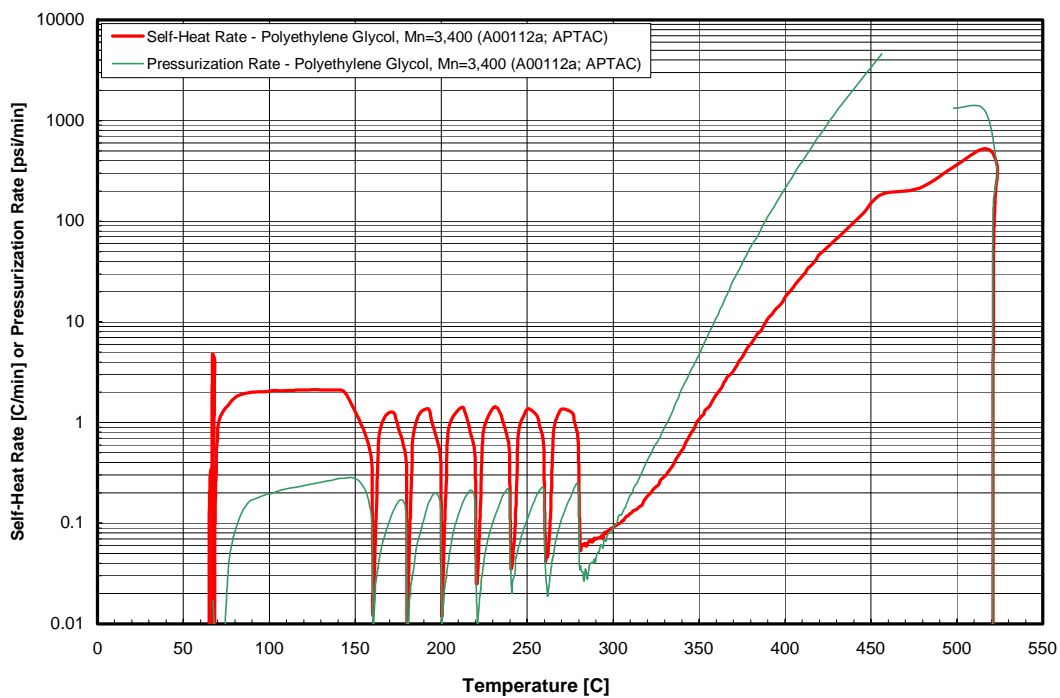
FIGURE 5b: CALORIMETRIC TESTING OF POLYETHYLENE GLYCOL - P vs. T
APTAC; Nitrogen
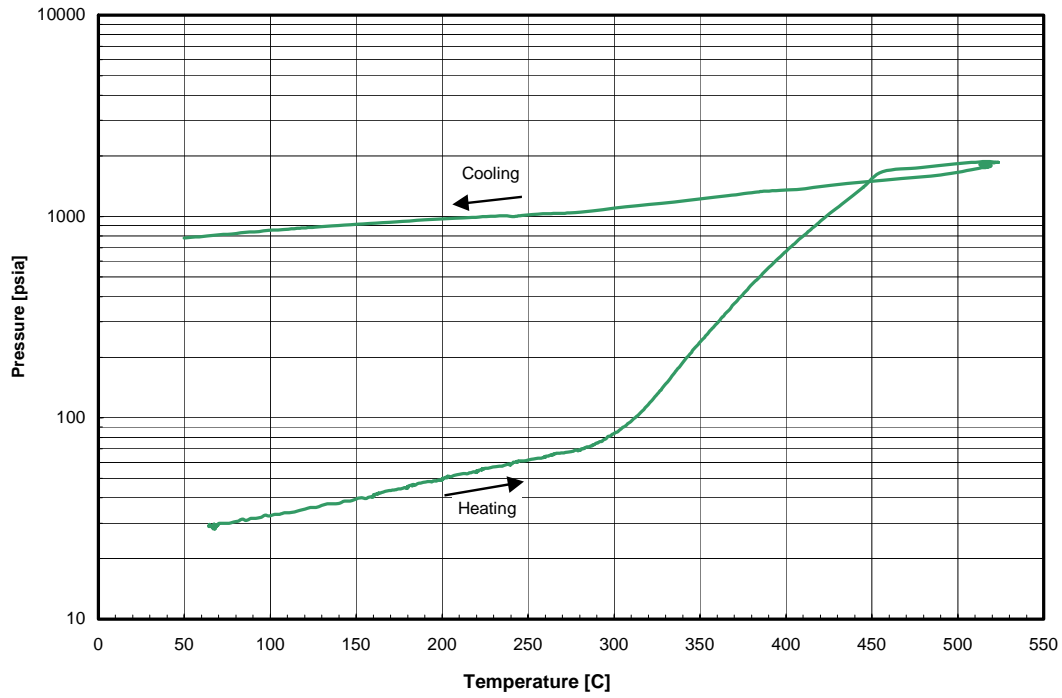
FIGURE 5c: CALORIMETRIC TESTING OF POLYETHYLENE GLYCOL
Netzsch DSC/TGA; Flowing Nitrogen
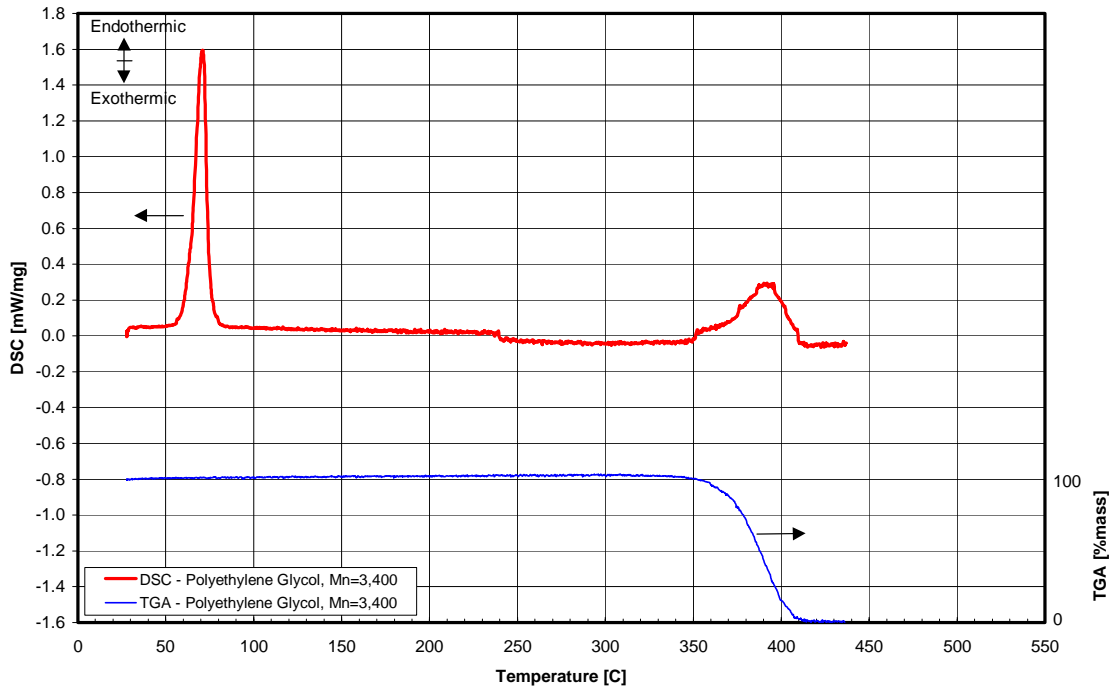
FIGURE 6a: CALORIMETRIC TESTING OF POLYPROPYLENE GLYCOL - T,P RATES
APTAC; Nitrogen
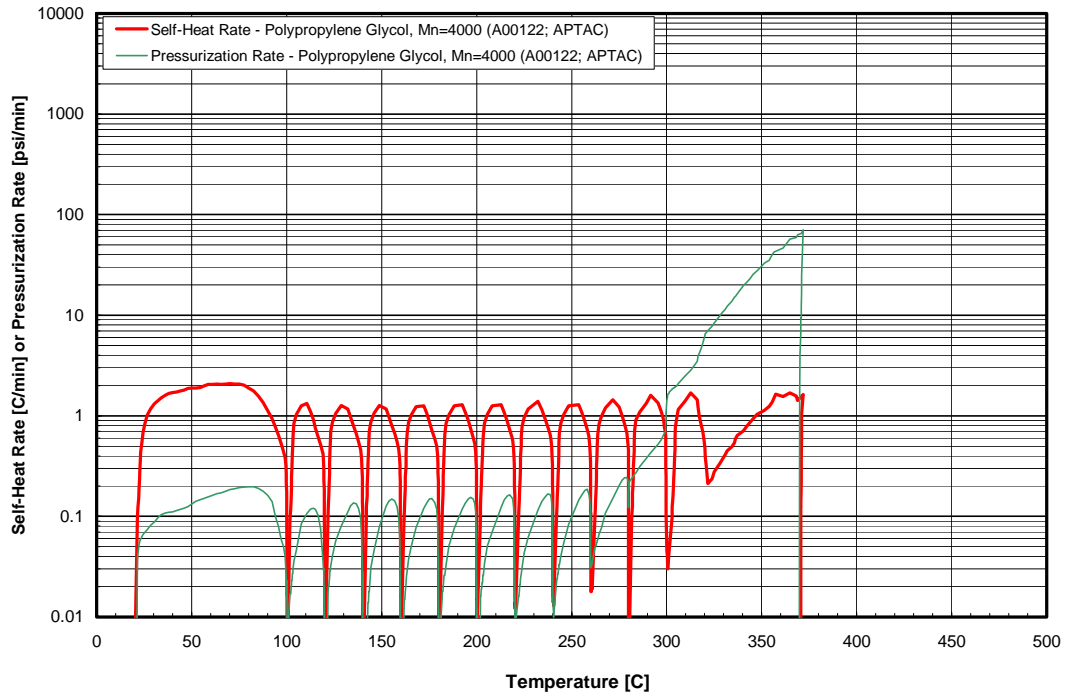
FIGURE 6b: CALORIMETRIC TESTING OF POLYPROPYLENE GLYCOL - P vs. T
APTAC; Nitrogen
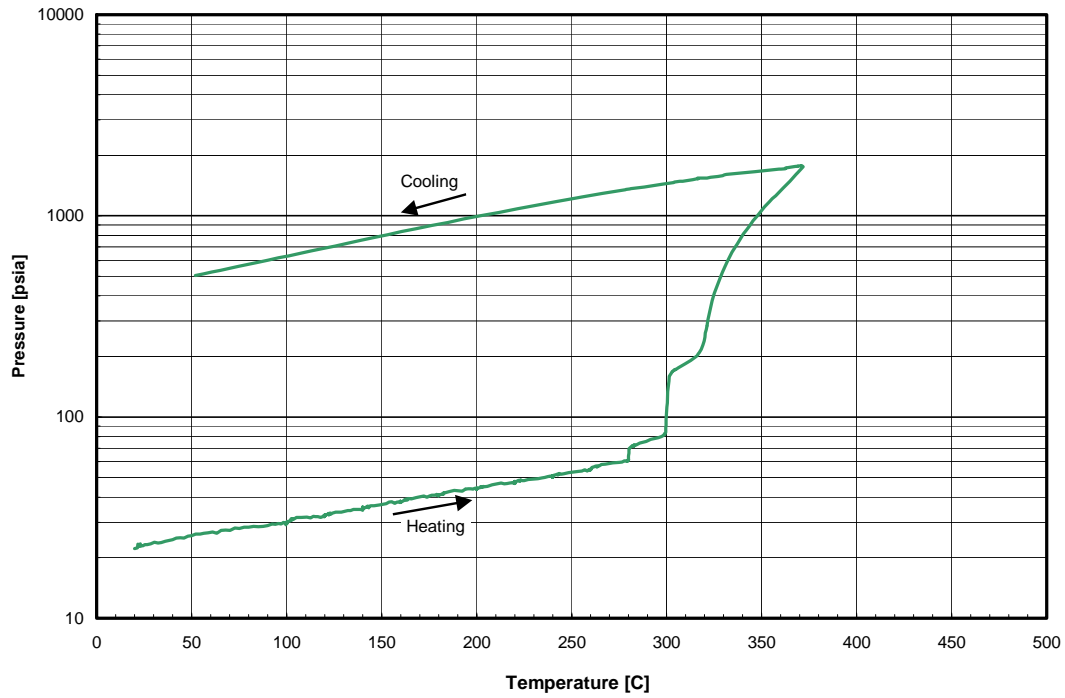
FIGURE 6c: DSC TESTING OF POLYPROPYLENE GLYCOL
Netzsch DSC/TGA; Flowing Nitrogen
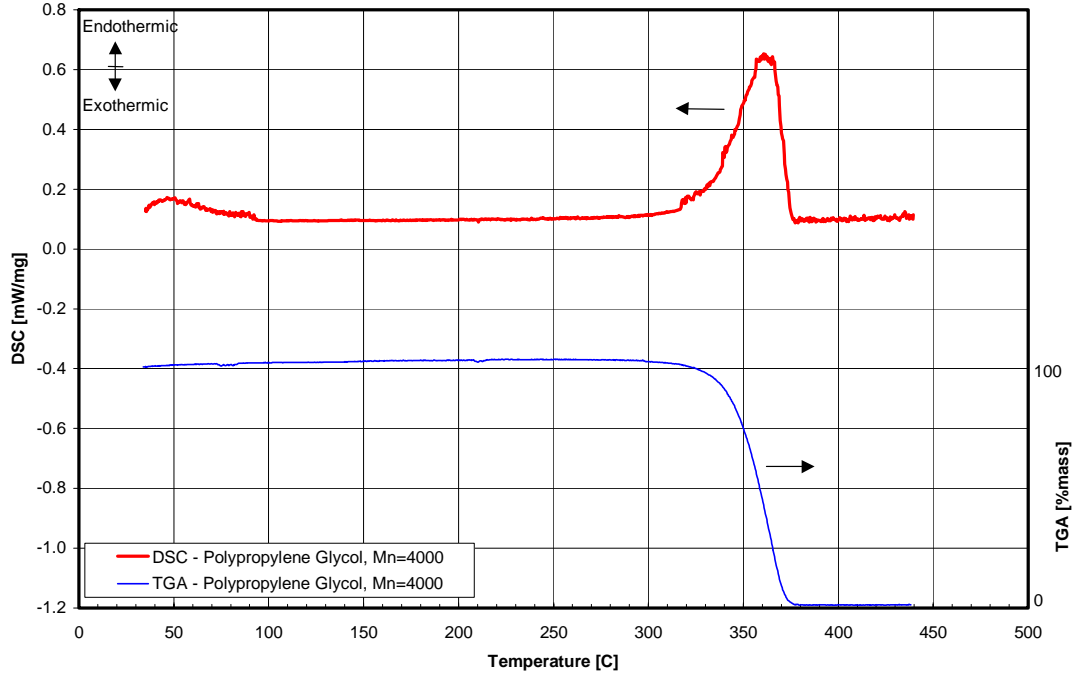
FIGURE 7a: CALORIMETRIC TESTING OF EPON HPT(R) RESIN 1050 - T,P RATES
APTAC; Nitrogen
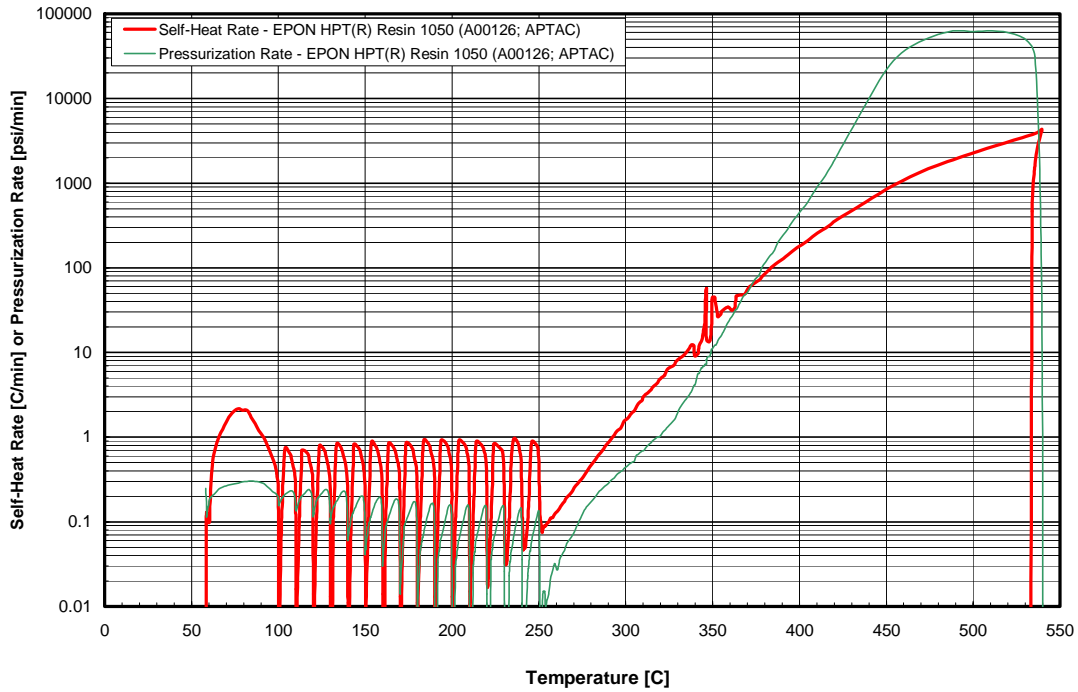
FIGURE 7b: CALORIMETRIC TESTING OF EPON HPT(R) RESIN 1050 - P vs. T
APTAC; Nitrogen
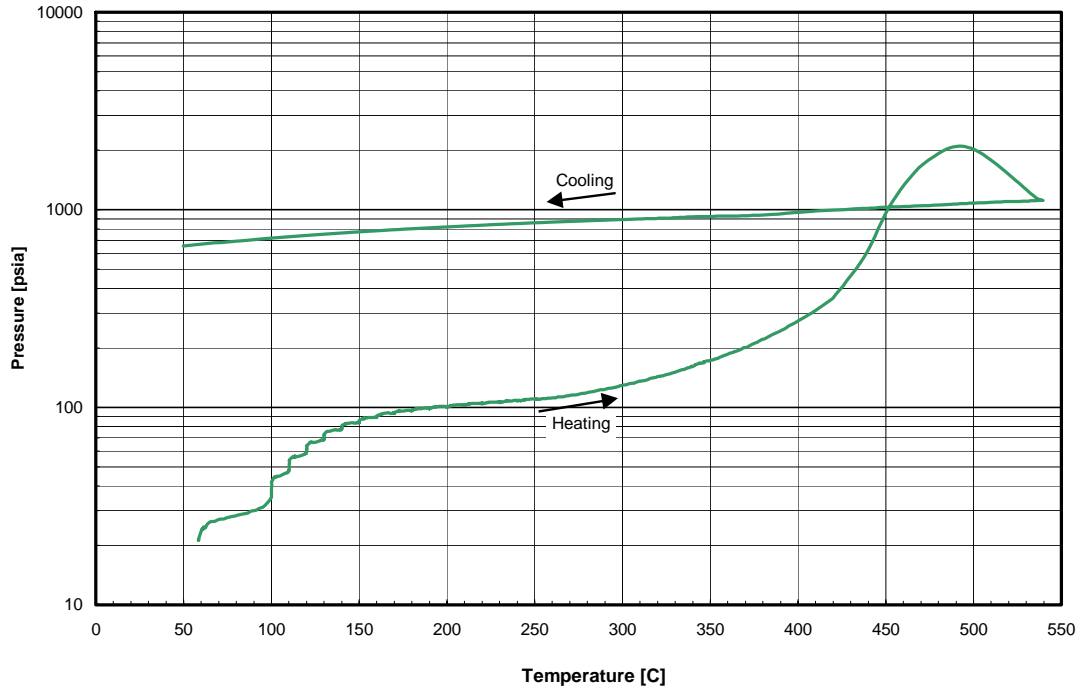
FIGURE 7c: DSC TESTING OF EPON HPT (R) RESIN 1050
Netzsch DSC/TGA, Flowing Nitrogen
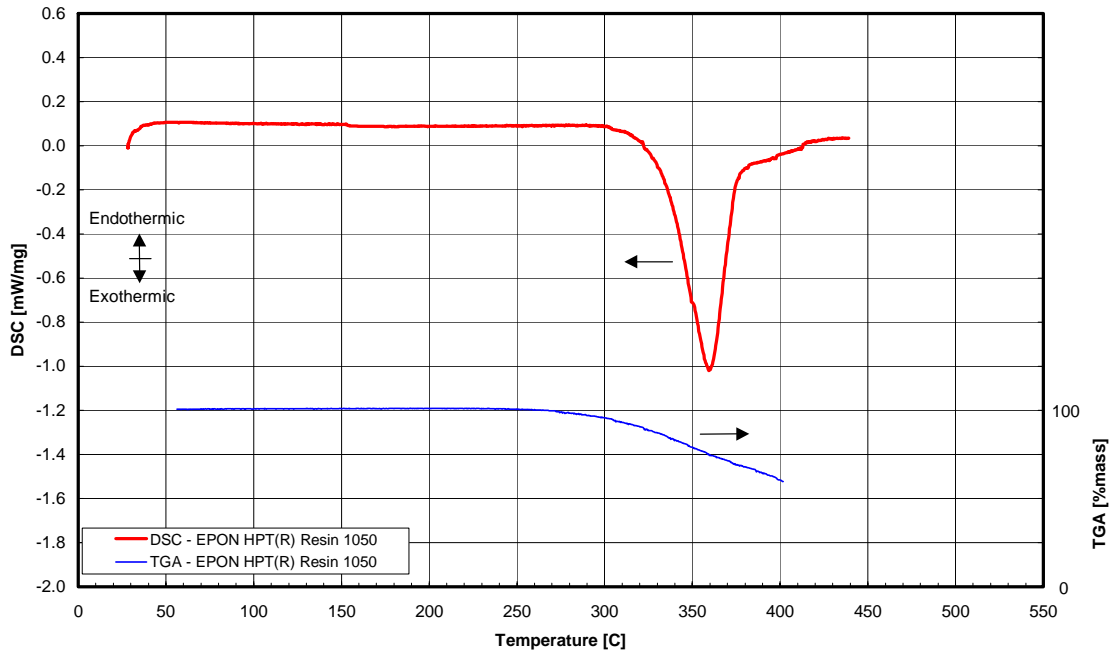
FIGURE 8a: CALORIMETRIC TESTING OF POLYVINYL METHYL KETONE - T,P RATES
APTAC; Nitrogen
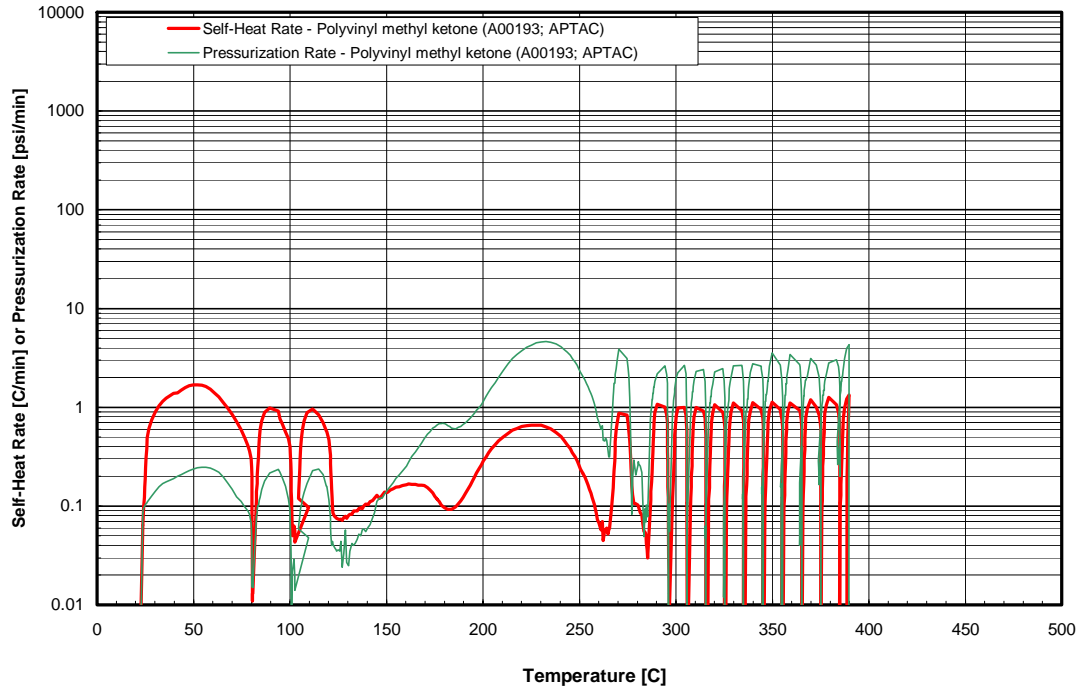
FIGURE 8b: CALORIMETRIC TESTING OF POLYVINYL METHYL KETONE - P vs. T
APTAC; Nitrogen
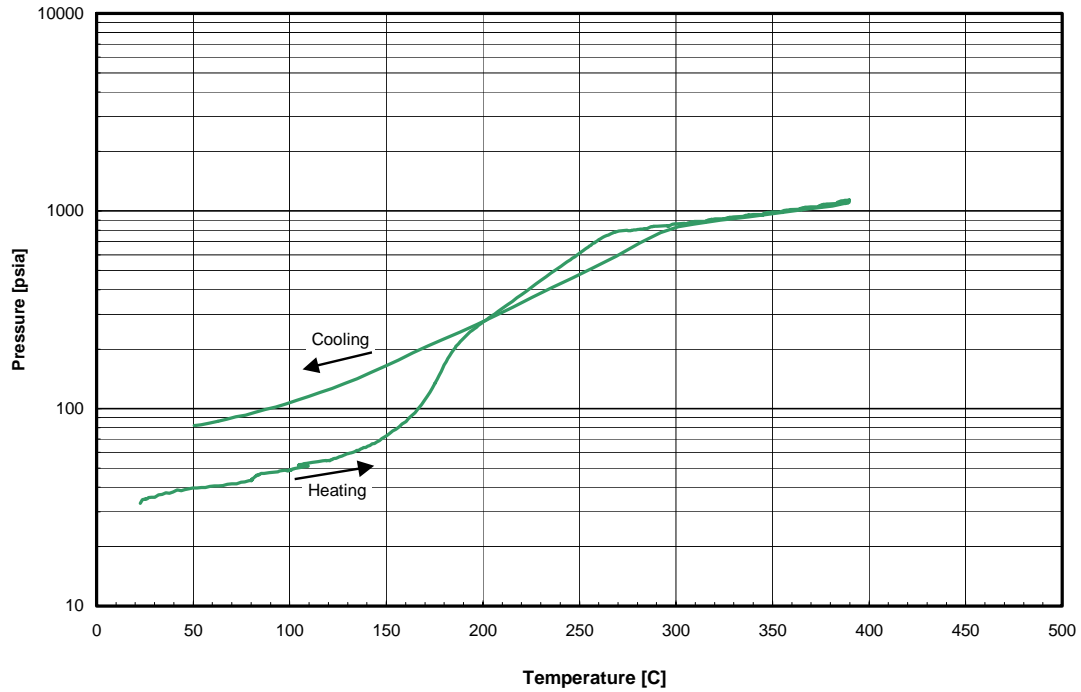
FIGURE 8c: CALORIMETRIC TESTING OF POLYVINYL METHYL KETONE
Netzsch DSC/TGA, Flowing Nitrogen
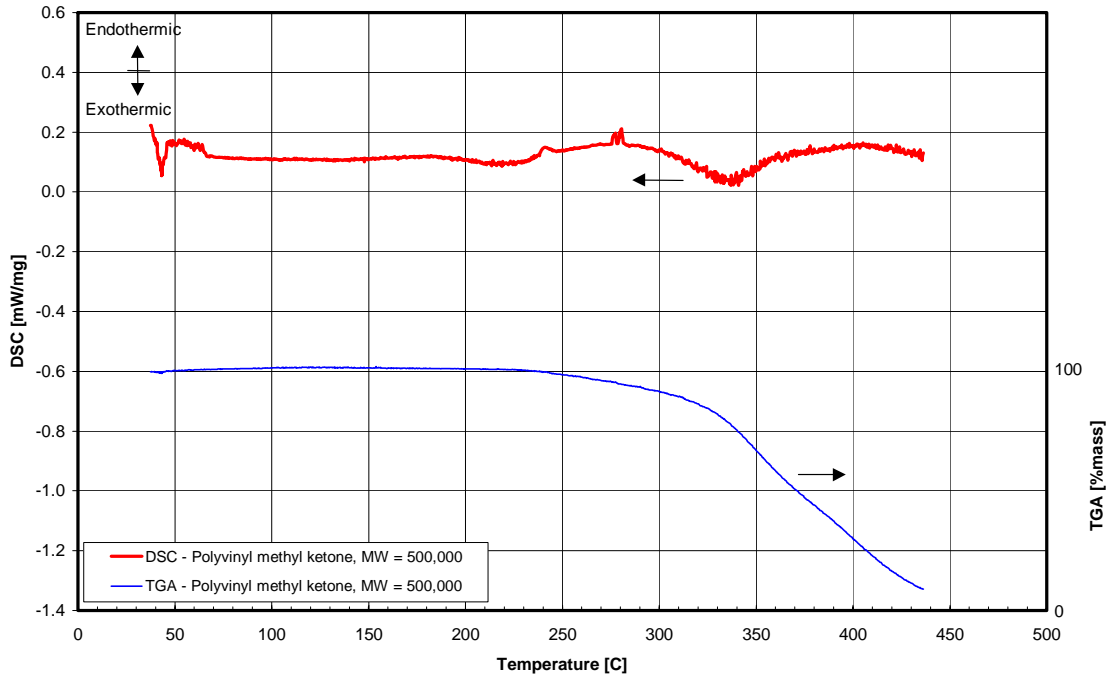
FIGURE 9a: CALORIMETRIC TESTING OF POLYVINYL PHENYL KETONE - T,P RATES
APTAC; Nitrogen
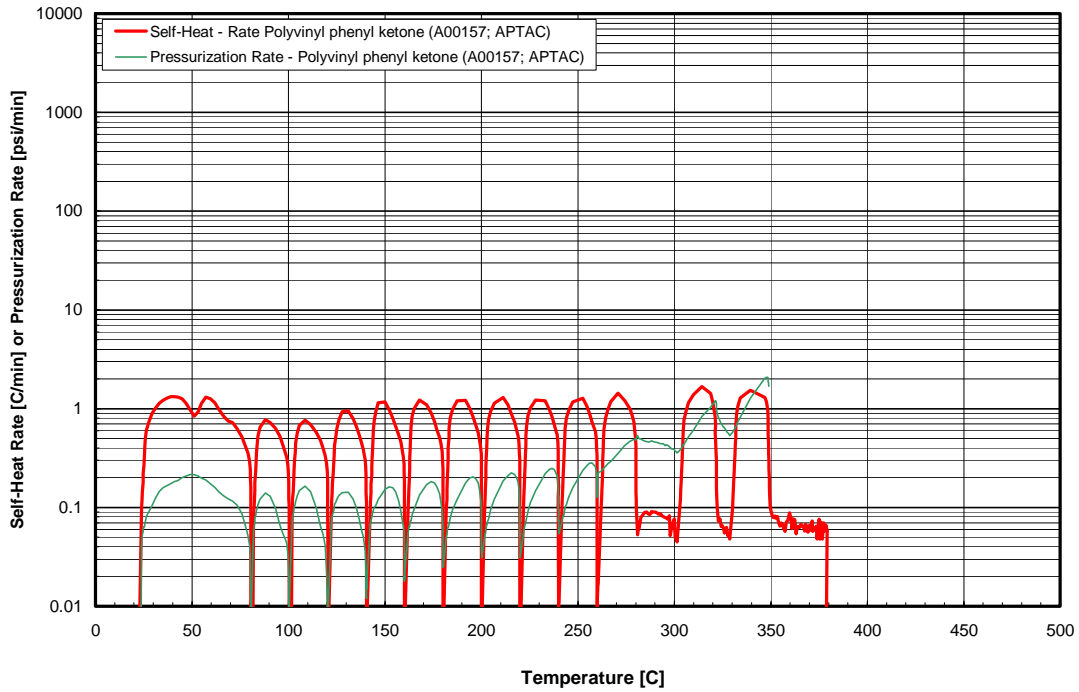
FIGURE 9b: CALORIMETRIC TESTING OF POLYVINYL PHENYL KETONE - P vs. T
APTAC; Nitrogen
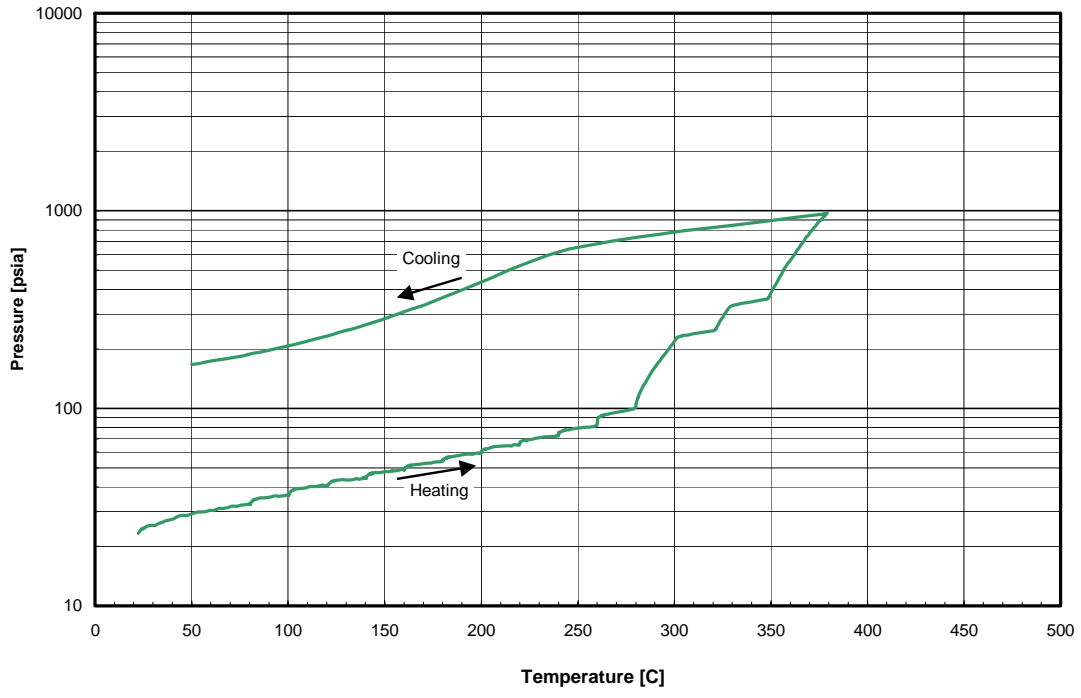
FIGURE 9c: CALORIMETER TESTING OF POLYVINYL PHENYL KETONE
Netzsch DSC/TGA; Flowing Nitrogen
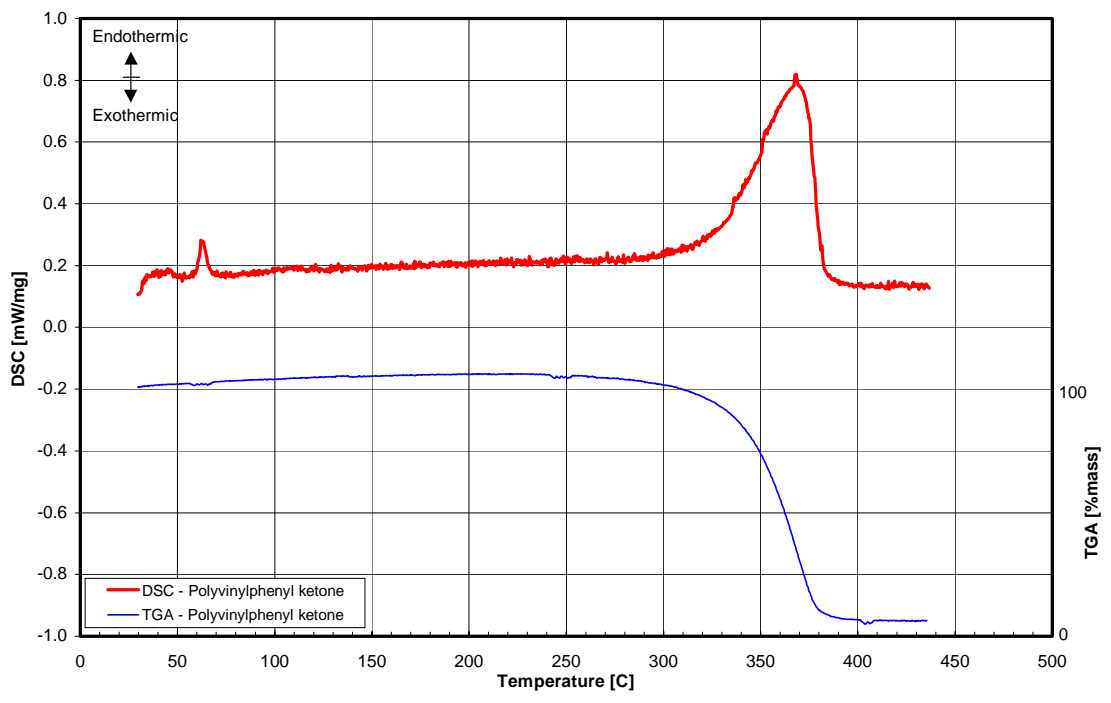
FIGURE 10a: CALORIMETRIC TESTING OF POLYACRYLIC ACID - T,P RATES
APTAC; Nitrogen

Legend:
- Self-Heat Rate - Polyacrylic acid, Mv=750M (A00147; APTAC)
- Pressurization Rate - Polyacrylic acid, Mv=750M (A00147; APTAC)

Y-axis: Self-Heat Rate [C/min] or Pressurization Rate [psi/min]
X-axis: Temperature [C]
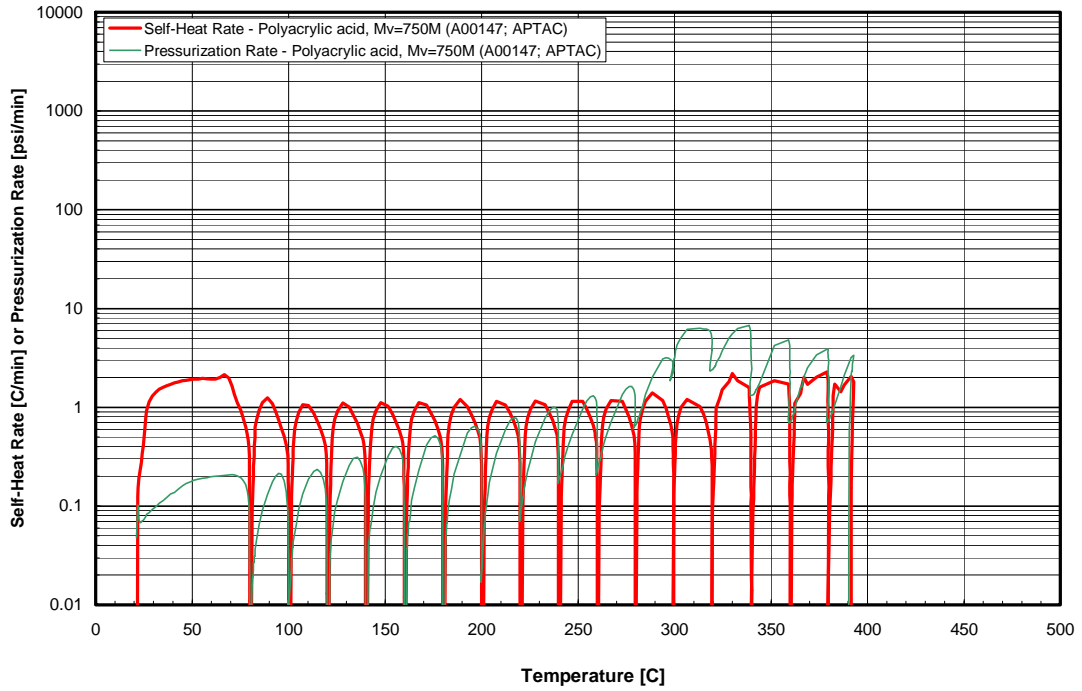
FIGURE 10b: CALORIMETRIC TESTING OF POLYACRYLIC ACID - P vs. T
APTAC; Nitrogen

Y-axis: Pressure [psia]
X-axis: Temperature [C]

Labels: Cooling, Heating
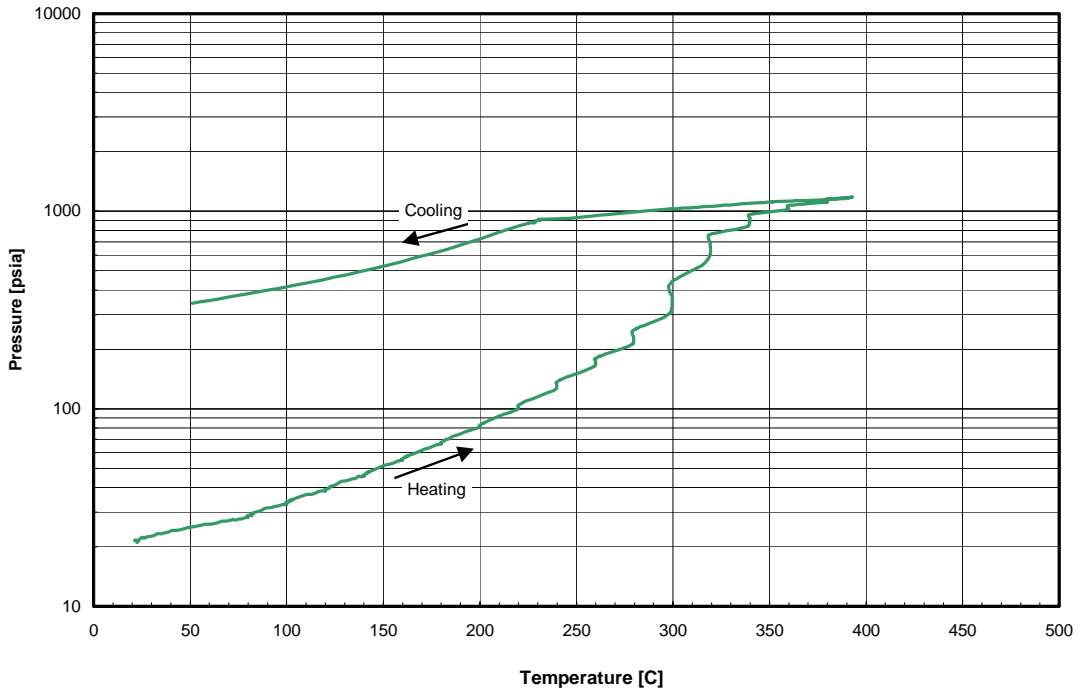
FIGURE 10c: CALORIMETRIC TESTING OF POLYACRYLIC ACID
Netzsch DSC/TGA, Flowing Nitrogen
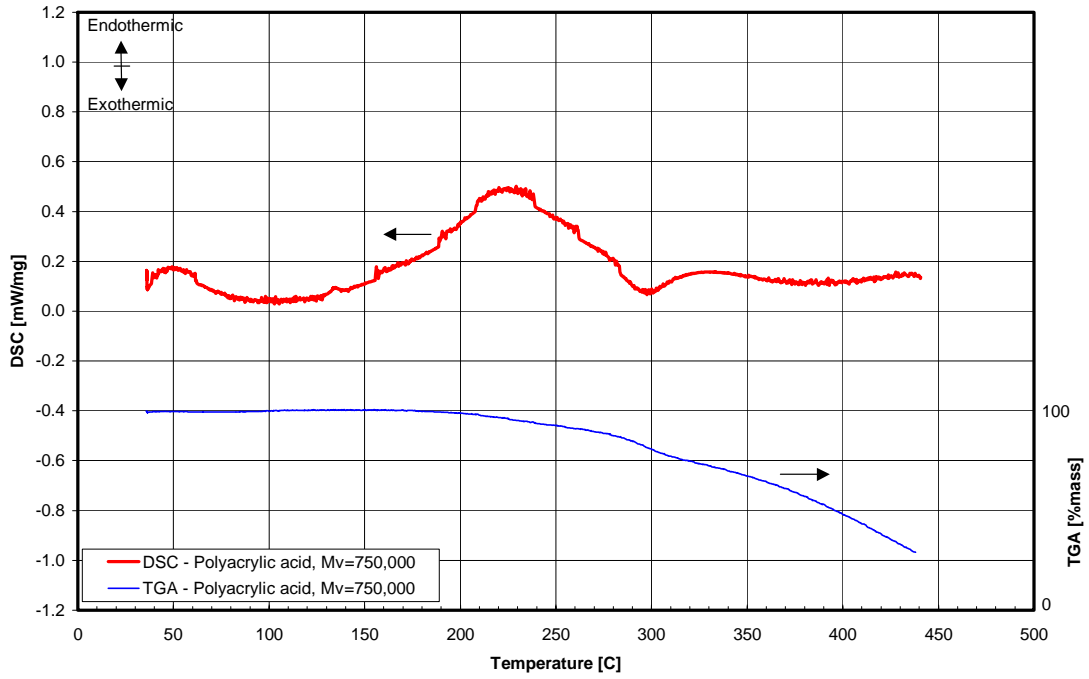
FIGURE 11a: CALORIMETRIC TESTING OF POLYETHYLENE TEREPHTHALATE - T,P RATES
APTAC; Nitrogen
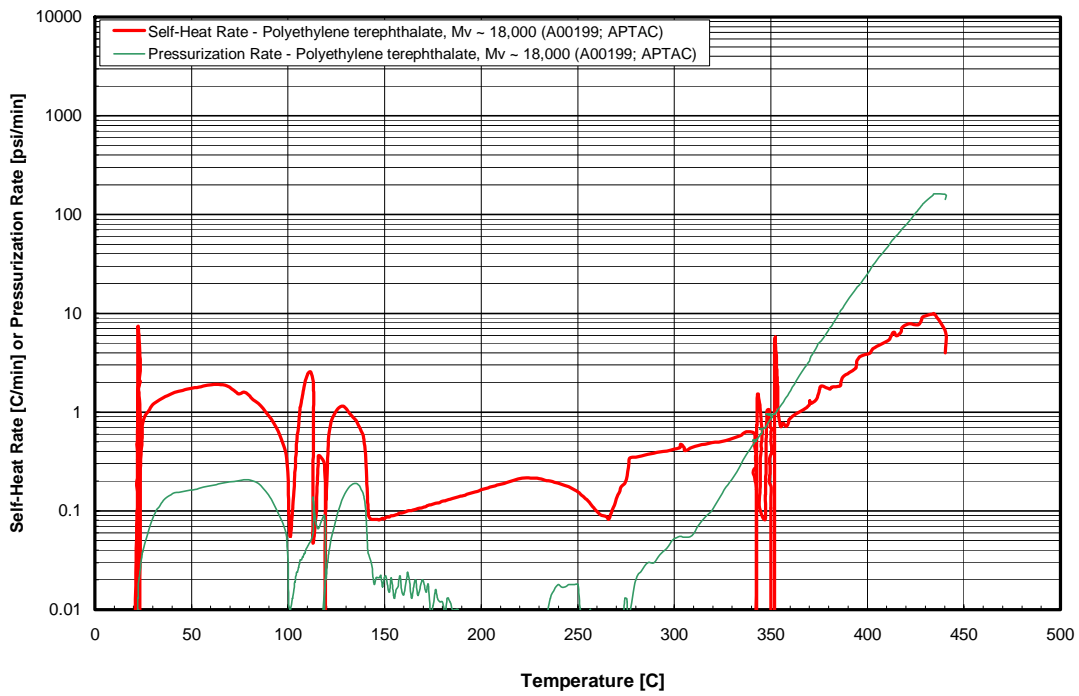
FIGURE 11b: CALORIMETRIC TESTING OF POLYETHYLENE TEREPHTHALATE - P vs. T
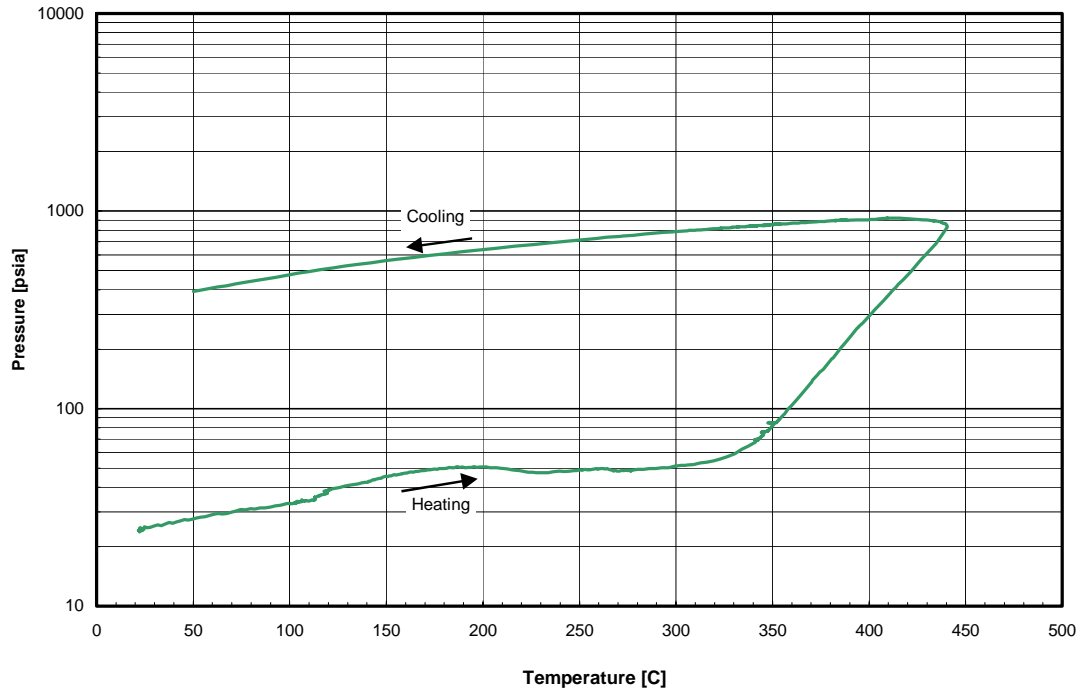**APTAC; Nitrogen**

FIGURE 11c: CALORIMETRIC TESTING OF POLYETHYLENE TEREPHTHALATE
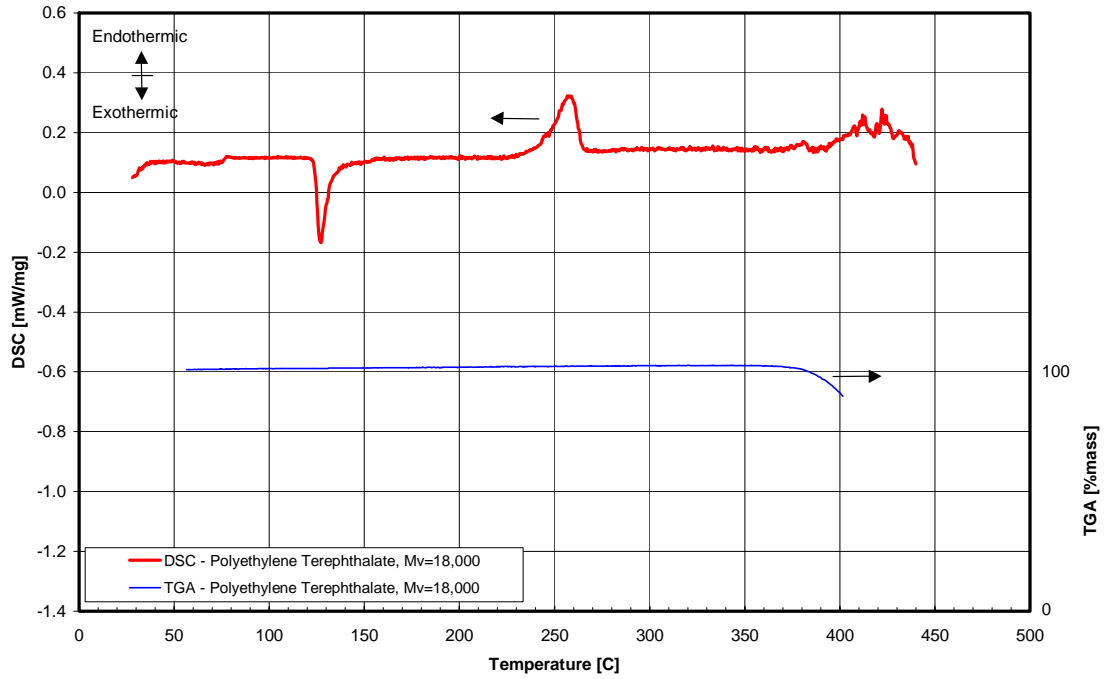**Netzsch DSC/TGA; Flowing Nitrogen**

FIGURE 12a: CALORIMETRIC TESTING OF POLYBISPHENOL ACETONE CARBONATE - T,P RATES
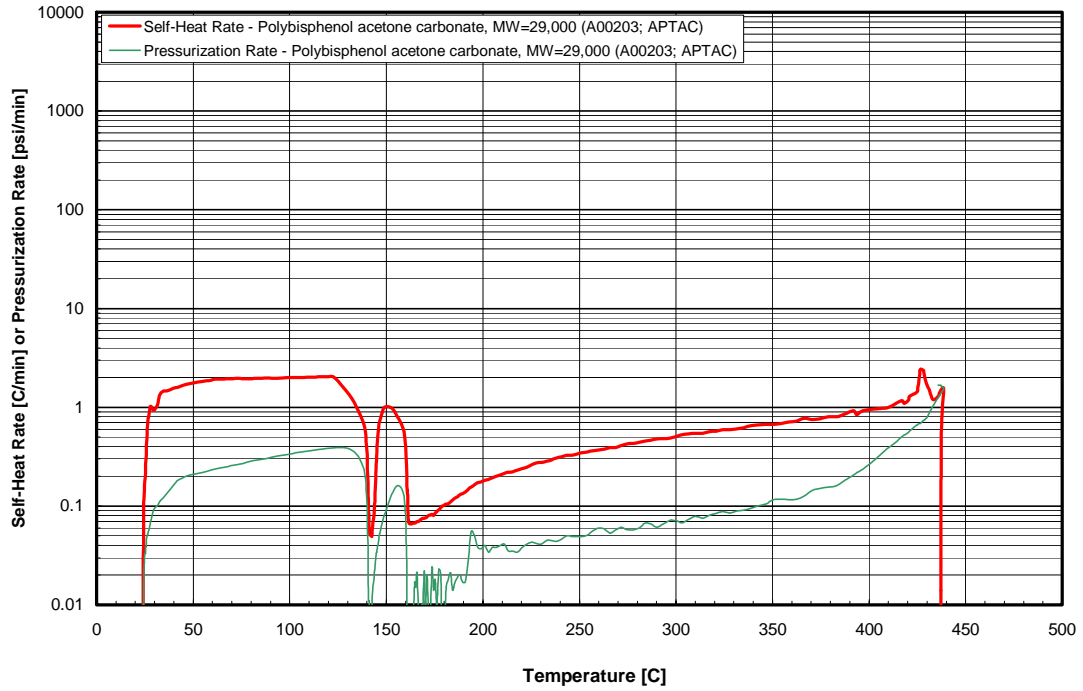**APTAC; Nitrogen**

FIGURE 12b: CALORIMETRIC TESTING OF POLYBISPHENOL ACETONE CARBONATE - T,P RATES
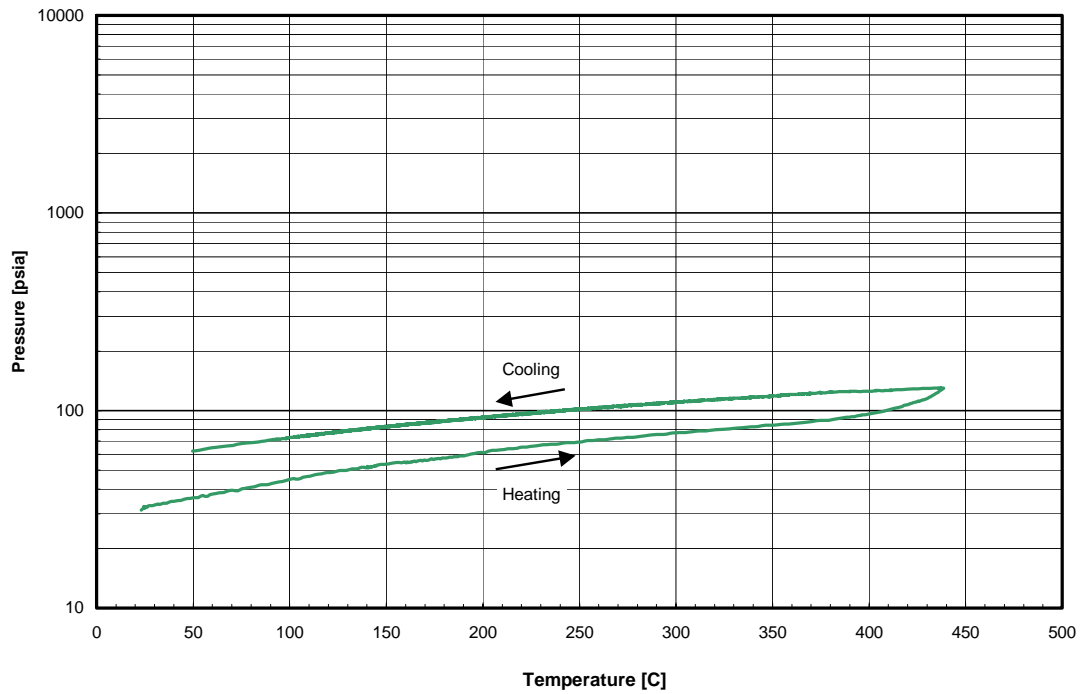**APTAC; Nitrogen**

FIGURE 12c: CALORIMETRIC TESTING OF POLYBISPHENOL ACETONE CARBONATE
Netzsch DSC/TGA; Flowing Nitrogen