

# DECARBOXYLATION OF SALTS OF AROMATIC CARBOXYLIC ACIDS AND THEIR ROLE IN CROSS-LINKING REACTIONS

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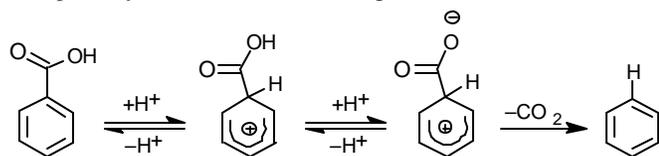
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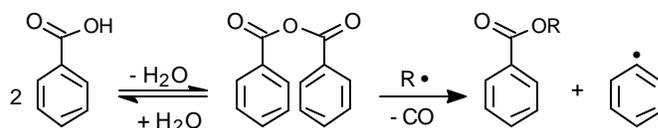
## Introduction

Carboxylic acids and alkali and alkaline earth metal salts of carboxylic acids play a significant role in controlling tar and liquefaction yields from the pyrolysis and liquefaction of low-rank coals.<sup>1,2,3</sup> Carboxylates are thought to be responsible for low temperature cross-linking reactions in pyrolysis and liquefaction, and cross-linking reactions have been correlated with loss of carboxyl groups and water.<sup>1,4</sup> Pretreatments such as demineralization or methylation reduce cross-linking, while ion-exchange of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, or Ba<sup>2+</sup> into demineralized low-rank coals increase cross-linking and CO<sub>2</sub> evolution in pyrolysis and liquefaction.<sup>5,6,7</sup> Alkali and alkaline earth metal cations also appear to change the aromatic/aliphatic composition of the tar in pyrolysis.<sup>8</sup> The reduction in tar and liquefaction yields by divalent cations has been attributed to cross-links formed between the carboxylic acids and the metal cations in the coal matrix.<sup>6</sup> In support of this theory, proton magnetic resonance thermal analysis spectroscopy has shown that the cation exchanged coals obtain a lower extent of fusion (i.e., they have a more rigid structure) during heating than the proton exchanged (i.e. acid) form, and the divalent cations have a greater effect than the monovalent cations.<sup>9</sup> The matrix density of the coals was found to follow the order: acid form < Na form < Ca form.

Despite the numerous studies on the impact of carboxylic acids and their salts on the pyrolysis, combustion, and liquefaction of low-rank coals, the decomposition reaction pathways, the primary reaction products, and the reaction kinetics are still poorly understood. To provide fundamental information on the decomposition of aromatic carboxylic acids and their salts, we have investigated the pyrolysis mechanisms of simple and polymeric model compounds containing aromatic carboxylic acids.<sup>10,11</sup> From these investigations, it was determined that decarboxylation of aromatic carboxylic acids, such as benzoic acid and bibenzylidene dicarboxylic acid, occurred primarily by an acid promoted ionic pathway that does not lead to a significant



amount of cross-linking (i.e., higher molecular weight products). However, in nondonor solvents (such as naphthalene), a small amount (<3 mol%) of cross-linked products, such as phenyl-naphthalene, was found.<sup>10b</sup> These cross-linked products arose from the condensation of the carboxylic acids to form aromatic anhydrides which can undergo a free radical induced



decomposition reaction to form an aryl radical that can abstract hydrogen or add to an aromatic ring to form arylated products. As predicted by this reaction pathway, the yields of CO were greater than CO<sub>2</sub>.<sup>10b</sup> Water was found to decrease the formation of cross-linked products by hydrolysis of the anhydride. Although anhydride formation was minor in the pyrolysis of these simple model compounds, anhydride formation was dominant in the pyrolysis of a polymeric model compound (poly-(1,3-xylylene-co-5-carboxy-1,3-xylylene) which contained 2.3 carboxylic acids per 100 carbons, which is similar to the concentration found in Beulah-Zap coal.<sup>10a</sup>

The pyrolysis of salts of carboxylic acids has briefly been investigated.<sup>11</sup> Sealed tube pyrolysis of the dipotassium salt of 1,2-(3,3'-dicarboxyphenyl)ethane at 400 °C for 30 min neat, in tetralin, or in naphthalene produced no products, and the starting material was recovered unchanged. Calcium benzoate was also found to be relatively stable at 400 °C (0.05 % conversion to benzene after 1 hr). Small amounts of water did not affect these sealed tube pyrolysis results. However, if benzoic acid was mixed with calcium benzoate, an increase in the rate of decarboxylation was observed that was proportional to amount of added salt. This observation is consistent with the ionic decarboxylation pathway previously described.

Thus, our initial investigations indicated that the carboxylate salts were relative stable at 400 °C. However, the decomposition temperatures and the reaction pathways of the simple carboxylate salts have not been adequately described in relation to coal pyrolysis. It is also unclear what would happen in a network structure, such as coal, in which the metal cations could hold the matrix together by ionic interactions. Therefore, in this investigation, the decomposition of alkali and alkaline earth metal salts of simple and polymeric model compounds containing aromatic carboxylic acids was investigated by TG-MS to determine their role in cross-linking reactions in low-rank coals. To establish a baseline of reactivity, sodium, potassium, and calcium benzoate were initially investigated, followed by the investigation of the copolymers of styrene and vinylbenzoic acid and their corresponding salts. Copolymers of styrene and vinylbenzoic acid were chosen since these are easy to prepare by free radical polymerization, and the decomposition pathways of polystyrene have been investigated.

## Experimental

Sodium and potassium benzoate were purchased from Aldrich (99%) and used as received. Calcium benzoate was prepared from ammonium benzoate and anhydrous calcium chloride as previously described.<sup>12</sup> Carboxy-terminated polystyrene was obtained from SP<sup>2</sup> ( $M_w = 9940$  and  $M_w/M_n = 1.06$ ). Copolymers of styrene and vinylbenzoic acid were prepared by free radical polymerization as previously described.<sup>13</sup> The mole fraction of vinylbenzoic acid in the copolymers was determined by titration in THF to the phenolphthalein end point with a standardized aqueous solution of NaOH. No precipitation was observed in the titrations. The molecular weight ( $M_w$ ) and polydispersity ( $M_w/M_n$ ) was determined

by GPC in THF relative to polystyrene standards. For poly(styrene-co-vinylbenzoic acid) with 2.3, 4.7, and 19.3 mol% vinylbenzoic acid, the  $M_w$  ( $M_w/M_n$ ) was 13,500 (1.8); 17,600 (2.1); and 11,970 (1.6), respectively. The salts of the acids were prepared by adding stoichiometric amounts of base (NaOH, KOH or  $\text{CaH}_2$ ) to a THF solution of the copolymer followed by precipitation into hexanes and drying. FTIR analysis confirmed the presence of the salts by disappearance of the free and hydrogen bonded C=O stretch at 1734 and 1688  $\text{cm}^{-1}$ , respectively.

TG-MS measurements were made on a TA Instruments Model 2050 thermogravimetric analyzer connected to a Balzers Thermostat mass spectrometer (0-300 amu) through a heated (200 °C) transfer line. The TGA temperature was calibrated by the Curie point of nickel and TG-MS performance was determined by decomposition of calcium oxalate. The swagelock interface between the TGA and transfer line was modified to minimize diffusion of oxygen into the system, and the interface was heated to 200 °C with a heating tape, which improved the transport of larger products, such as benzophenone, to the MS. Samples were weighed in a platinum pan and the samples were purged with argon ( $100 \text{ mL min}^{-1}$ ) until the oxygen levels stabilized (ca. 1-3 h, typically  $<50 \text{ ppm O}_2$ ). It was found that residual oxygen would affect the final residue yields by gasifying the residue. The samples were heated at  $5 \text{ °C min}^{-1}$  from room temperature to 800 °C. Initially the weight of TG-MS samples were between 15-30 mg, and the MS was run in the scan mode (2-200 amu) to determine which masses were changing during the pyrolysis. Then, small samples (1-3 mg) were run, and the MS was run in the SIM mode, which provided higher sensitivity. All measurements were repeated, and the transition temperatures and residue yields were reproducible. TGA curves were analyzed with Universal Analysis software from TA Instruments, and the mass spectrometry data analyzed with the Balzers software.

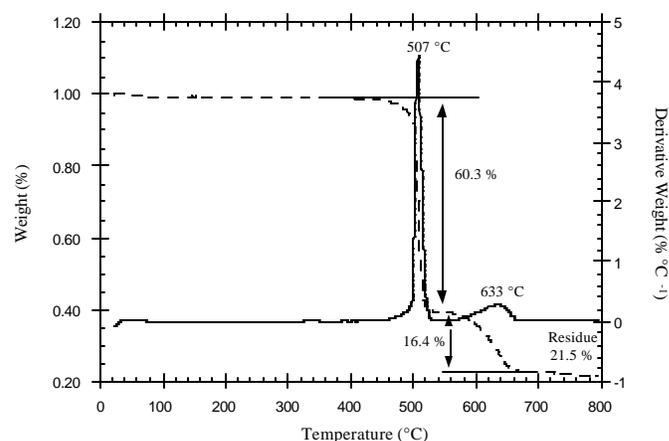
Sodium and potassium benzoate (50-70 mg) were heated at  $5 \text{ °C min}^{-1}$  in the TGA until 500 °C and cooled to room temperature. The charred solids were removed and dissolved in pyridine with chlorotrimethylsilane. The reaction mixtures were analyzed on a Hewlett Packard 5890 Series II Plus gas chromatograph employing a J&W DB-5, 5% diphenyl-95% dimethylpolysiloxane capillary column (30 m x 0.25 mm id. with 0.25  $\mu\text{m}$  film thickness). Mass spectra were obtained at 70 eV with a Hewlett Packard 5971A/5972 mass selective detector and a capillary column identical to that used for GC-FID analysis. Products were identified by comparing the retention times and/or mass spectral fragmentation patterns from authentic samples or from the NIST mass spectral library.

## Results and Discussion

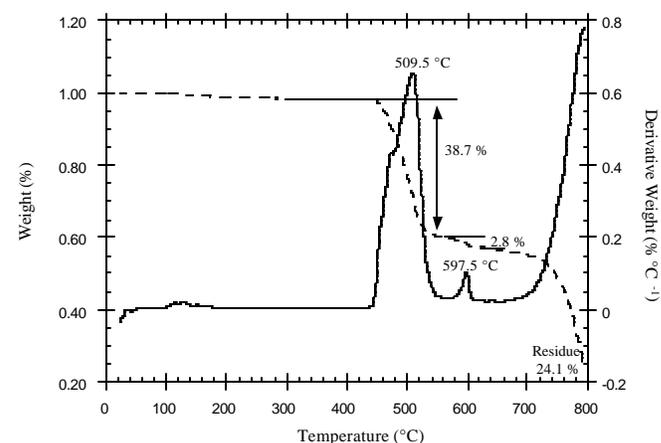
**Pyrolysis of benzoic acid salts.** The TG-MS of the calcium, potassium, and sodium salt of benzoic acid was investigated at a heating rate of  $5 \text{ °C min}^{-1}$  under a flow of argon ( $100 \text{ mL min}^{-1}$ ) to determine the role of the metal cation on the decomposition temperature. The TGA traces of the three salts are shown in **Figures 1-3**, and the evolved products were monitored by a mass spectrometer. All three samples show a major weight loss at  $509 \pm 2 \text{ °C}$ , although the shape of the derivative peaks is different. For the potassium and sodium benzoate, the yield of residue formed at 800 °C was found to be dependent on the sample size, but the material remaining after the first transition (at 509 °C) was independent of sample size. The major ions from the evolved products formed

during this transition for the potassium and sodium benzoates are  $m/z$  28 (CO), 44 ( $\text{CO}_2$ ), 77 (phenyl) and a small amount of  $m/z$  154 (biphenyl), 150, and 105. In addition to these ions, calcium benzoate showed a loss of  $m/z$  182 (benzophenone) and a major 105 fragment ion. Although the first transition for the three salts occurs at the same temperature, it is clear that calcium benzoate undergoes a different set of reactions from the sodium and potassium benzoates based on the evolved products and weight losses.

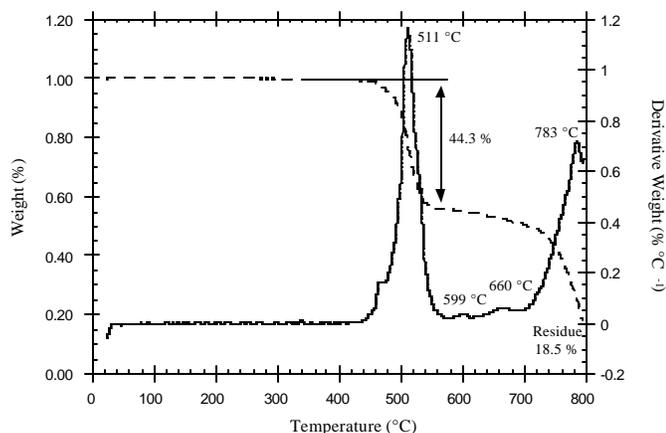
Although calcium exchanged low-rank coals produce low tar and liquefaction yields, the reaction pathway of calcium salts, such as calcium benzoate, has not been recognized by the coal community. The decomposition of calcium salts of aliphatic carboxylic acids has been previously investigated by Hites and Biemann.<sup>14</sup> It was shown that these salts decompose at 500 °C by a free radical pathway to produce ketones, alkanes, and alkenes. Calcium carbonate was also produced as a byproduct that can undergo additional degradation to calcium oxide and  $\text{CO}_2$ .



**Figure 1.** TGA and DTG of calcium benzoate.

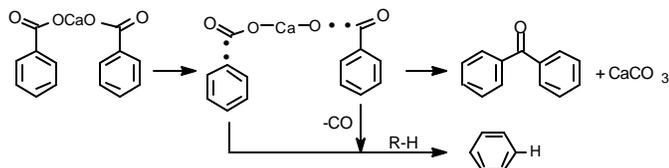


**Figure 2.** TGA and DTG of potassium benzoate.



**Figure 3.** TGA and DTG of sodium benzoate.

Pyrolysis of calcium benzoate at 500 °C was reported to produce equal amounts of benzophenone (from coupling of the benzoyl and phenyl radical) and benzene (from decarbonylation of the benzoyl radical followed by hydrogen abstraction by the phenyl radical).<sup>14</sup> A trace amount of biphenyl and 9-fluorene was also formed which was consistent with reaction pathways proposed for the pyrolysis of aliphatic calcium salts. TG-MS analysis of calcium benzoate was consistent with this proposed reaction pathway. Calcium benzoate decomposes to benzophenone and benzene, which will sublime, and calcium carbonate. This should produce a



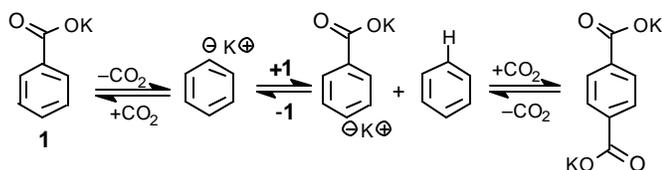
64.5% weight loss for the first transition. A 60.3 % weight loss was observed which was in good agreement with expectations. The evolved gases during this transition contained  $m/z$  44 ( $\text{CO}_2$ ), 77 (fragment ion from benzene and benzophenone), 105 (fragment ion of benzophenone), and small amounts of  $m/z$  154 (biphenyl) and 182 (benzophenone). The small intensity of the benzophenone ion was initially concerning, but it was discovered that benzophenone was inefficiently transferred to the mass spectrometer. The ion intensity of benzophenone was determined by sublimation of an authentic sample from the TGA. A small 182 ion was observed but the dominant ion was the  $m/z$  105 fragment ( $\text{PhCO}$ ). Heating the interface between the TGA and the mass spectrometer transfer line to 200 °C improved the intensity of the ions. A similar intensity pattern for  $m/z$  182 and 105 was observed in the TG-MS of the calcium benzoate. The second transition in the TGA trace should be from the decomposition of the calcium carbonate to calcium oxide which should leave 19.9 wt% residue. The mass spectrum only showed  $\text{CO}_2$  evolving (and a trace of  $\text{CO}$ ) during this second transition and 21.5 wt% residue was found.

Thus, decomposition of calcium benzoate occurs by a free radical pathway, as previously reported.<sup>14</sup> Cross-links can be formed between aromatic rings via ketone bridges or through addition of an aryl radical to neighboring aromatic rings. Addition of a hydrogen

donor solvent, such as tetralin, should intercept the free radicals and reduce cross-linking. However, it may not impact the intramolecular coupling to form benzophenone, but hydrogen donor solvents reduce diaryl ketones to the diarylmethanes, which also act as low temperature cross-links.<sup>15</sup> Manion, McMillen, and Malhotra briefly investigated the pyrolysis of calcium benzoate at 400 °C for 1 h in tetralin (16±12% conversion).<sup>12</sup> A small amount of decarboxylation (2.1 mol%) was observed at these lower temperatures, and benzene was the only observed product (i.e., no coupling products). However, decarboxylation of calcium anisate at 400 °C for 1 h was quantitative and ca. 5 mol% coupling products were observed (xanthene and benzylphenol). Similar coupling products were observed for the pyrolysis of the calcium anisate neat or diluted (10–fold) with naphthalene or tetralin. Thus, the hydrogen donor solvents did not appear to impact the coupling reactions, but at such high conversions, it is sometimes difficult to determine the primary reaction products. Therefore, this system should be reexamined at lower conversion to determine the origin of the cross-linked products.

The weight loss curves for decomposition of the sodium and potassium benzoates (**Figures 2 and 3**) are different than the calcium benzoate. Both have a shoulder on the low temperature side of the first transition and no benzophenone was observed and only a trace of  $m/z$  105 was found. If the same reaction pathway was occurring as for the calcium benzoate, sodium and potassium carbonate would be formed and the initial weight loss would be 63.2 and 56.9 wt% for the sodium and potassium benzoates, respectively. The first transitions had a smaller weight loss than predicted with 44.3 and 38.7 wt% loss for the sodium and potassium benzoates, respectively. To gain insight into the reaction pathways, potassium benzoate heated in the TGA at 5 °C  $\text{min}^{-1}$  to 500 °C, and the products in the residue were analyzed by GC and GC-MS. The recovered sample (84.6 wt%) was charred, and the sample appeared to have melted and expanded (most likely due to gas evolution). This residue was dissolved in chlorotrimethylsilane/pyridine and analyzed by GC and GC-MS. Benzoic acid (78.4 mol%), phthalic anhydride (10.8 mol%), isomers of benzenedicarboxylic acid (6.5 mol%), and two isomers of phenylbenzoic acid (4.3 mol%) were found. The experiment was repeated but the sample temperature was increased to 550 °C (38.1 %wt loss, 61.9 % residue). The only significant product that was observed in the 550 °C residue was benzenedicarboxylic acids. The products from heating sodium benzoate to 500 °C at 5 °C  $\text{min}^{-1}$  was also analyzed (95.0 % residue). Compared to potassium benzoate, sodium benzoate had a smaller conversion (5.0 %wt compared to 15.4 %wt loss), but similar products were formed (phthalic anhydride, benzenedicarboxylic acids, and two isomers of phenylbenzoic acid).

Disproportionation of potassium benzoate is known to occur in the presence of a catalytic amount of cadmium salt to produce benzene and terephthalic acid. The industrial scale thermal rearrangement or disproportionation of alkaline salts of aromatic acids to symmetrical diacids in the presence of a metallic salt is known as the Henkel Reaction.<sup>16</sup> The mechanism for this reaction is generally believed to involve decarboxylation to the aryl anion, hydrogen abstraction from the aromatic ring of another salt, followed by reaction of the resulting anion with  $\text{CO}_2$ .<sup>17</sup> The



reaction can occur with the sodium or lithium salts, but the reaction requires higher temperatures and yields are lower. Since the aryl anion has to react with the  $\text{CO}_2$  trapped in the melt, reactions in closed systems or under  $\text{CO}_2$  provide higher yields. Isomerization of potassium phthalate under nitrogen lowers the yield of terephthalate and precoking products such as fluorene terphenyl, and 9-phenylfluorene were observed.<sup>17a</sup> These products are most likely formed by free radical pathways. There is a second small transition for both samples at ca. 598 °C, and the same ions were observed in the mass spectrum as were found in the first transition. At temperatures >700 °C, another significant transition was detected, and only CO and  $\text{CO}_2$  were observed in the mass spectrum. Sodium and potassium carbonates are known to decompose to the oxide and release  $\text{CO}_2$  near and at their melting point (851 °C<sup>18</sup> and 900 °C,<sup>19</sup> respectively). There could also be a small amount of gasification catalyzed by the metal ions since trace amounts (=50 ppm) of oxygen are in the system. Alkali and alkaline earth metals have also been found to evaporate in the pyrolysis of brown coals at 600 – 800 °C which could also be responsible for some of the high temperature weight loss.<sup>20</sup> Thus, it is proposed that the potassium and sodium benzoates decompose by an uncatalyzed Henkel Reaction (i.e., disproportionation to benzenedicarboxylic acid and benzene) and a free radical reaction pathway that leads to cross-linked products and char. We plan to investigate the free radical reaction pathways in more detail in the future.

**Pyrolysis of copolymers and their salts.** In coal, the metal cations are proposed to cross-link the coal structure. Thus, a series of copolymers of styrene and vinylbenzoic acid were prepared in which the concentration of vinyl benzoic acid was varied. The thermal decomposition of the acids and their salts was investigated to determine the reaction pathways of the carboxylates in a confined matrix.

The TGA of a series of styrene-*co*-vinylbenzoic acid polymers was run at 5 °C min<sup>-1</sup> to 800 °C, and the data summarized in Tables 1 and 2. As the acid content of the copolymer increased, the residue at 600 °C increased. A similar trend in the residues was also found at 800 °C. The TGA trace of poly(vinylbenzoic acid) had three regions of weight loss. The origin of the first transition (180 °C) is not clear, but it does not come from water loss. The second transition at 338 °C is from water loss. From our previous studies, this is in the region where carboxylic acids condense to form anhydrides and expel water.<sup>10a</sup> The transition at 447 °C is from depolymerization of the polystyrene backbone (unzipping reaction that predominately forms monomer).<sup>21</sup> The methyl esters of the copolymers, prepared by reaction of the copolymers with diazomethane, cleanly depolymerize in the TGA experiment, and no residue (<0.1 wt%) was found at 600 °C. This highlights that the acids are responsible for the formation of the nonvolatile residue (which are most likely cross-linked products from arylation reactions).

**Table 1. TGA Data from the Polymers and Copolymers**

Compound	Transition°	% wt loss	Residue at
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	C		600 °C (wt%)
PS	410	99.7	0.2
P(S- <i>co</i> - 2.3% VBA)	404	99.1	0.4
P(S- <i>co</i> -4.7% VBA)	405	98.8	0.5
P(S- <i>co</i> -19.3% VBA)	417	93.5	4.6
PVBA	180	4.7	29.3
	338	6.4	
	447	61.3	

P = Poly, S= Styrene, VBA = Vinylbenzoic acid

The TGA data from the sodium salts of the copolymers is summarized in Table 2. The salts tended to contain water of hydration and most samples (except the 23 mol% acid) showed water loss between 110-130 °C. The next major transition for the salts (ca. 405 °C) tended to be slightly broader than that for the free acid. The polystyrene appeared to depolymerize at the same temperature as that found for the free acid, but as the concentration of salt increased, a shoulder was observed on the high temperature side of the polystyrene degradation. The peak temperature for this transition was similar to that observed from sodium benzoate. Therefore, the copolymers behave almost like pyrolysis of two separate samples, polystyrene and sodium benzoate. The salt of the copolymers also produced more residue than the acid form of the polymers, and the residue increases with the concentration of carboxylate salt. For the sodium salt of poly(vinylbenzoic acid), a major weight loss transition was observed at 511 °C, which was similar to that observed from the TGA of sodium benzoate. At this temperature, the depolymerization temperature of polystyrene has been exceeded, but the salts of the monomer are not volatile, and the products remain until decarboxylation occurs. The potassium salt of poly(vinylbenzoic acid) appears to have a slightly lower transition temperature (482 °C) than the sodium salt (511 °C). We are currently preparing and analyzing the potassium and calcium salts of these copolymers and this data will be presented.

**Table 2. TGA Data from the Sodium Salt of Poly(styrene-*co*-vinylbenzoic acid)**

Compound	Transition° C	% wt loss	Residue 600 °C (wt%)
P(S- <i>co</i> - 2.3% VBA) Na salt	404	91.3	7.9
P(S- <i>co</i> -4.7% VBA) Na Salt	409 493	87.6 1.2	6.4
P(S- <i>co</i> -19.3% VBA) Na Salt	116 416 513	9.2 49.3 8.6	33.0
PVBA Na Salt	511	22.8	58.9
PVBA K Salt	482	34.5	61.2

## Conclusion

The reaction pathways for the decomposition of salts of aromatic carboxylic acids was investigated by TG-MS. The calcium, potassium, and sodium benzoates undergo major weight losses at 509 ± 2 °C. Calcium benzoate undergo a free radical decomposition reaction to form benzophenone, benzene, and calcium carbonate as

the major products. Sodium and potassium benzoate undergoes an uncatalyzed Henkel Reaction to form dicarboxylic acids and aromatic hydrocarbons and a free radical reaction to form coupled aromatic products and char.

Copolymers of styrene and vinylbenzoic acid were prepared and analyzed by TG-MS. As the content of carboxylic acids in the copolymers increased, the residue, found at 600 °C, increased. The copolymers of styrene and the sodium salt of vinylbenzoic acid formed more residue than the acid form of the polymers. The copolymers behaved independently and showed two transitions: one for the polystyrene and one for the decarboxylation of the salt. Qualitatively, the decomposition pathways of the salts in the polymer matrix appear to be similar to that of the simple benzoate salts. However, the mass spectral data from the TG-MS of the copolymers and their salts needs to be investigated in more detail to determine if there is any difference in the product distributions. Also, the impact of a divalent cation, such as calcium, on cross-linking reactions need to be determined.

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