# Determination of sodium polyacrylate by pyrolysis–gas chromatography

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## Abstract

The use of sodium polyacrylate superabsorbent polymers continues to grow for the disposable baby and adult diapers market. The fate of these materials in the environment is of continuing interest for the producers and users of these polymers. A method was previously described for the determination of polyacrylic acid in environmental samples after derivatization by pyrolysis–gas chromatography (GC) and by size-exclusion chromatography. However, much of the polymer exists in the neutralized form as sodium polyacrylate which interferes with the derivatization procedures. This paper describes a pyrolysis–GC technique that can be applied to the determination of sodium polyacrylate in the environment without derivatization. Proposed mechanisms for the pyrolysis of the polymer are included as well as identification of the primary pyrolytic products.

## 1. Introduction

As discussed in a previous paper [1] polyacrylic acid may be determined in environmental samples by pyrolysis–gas chromatography (Py–GC) after derivatization of the polymeric acid to the methyl ester. However, in most commercial forms, polyacrylic acid actually exists as the sodium salt or sodium polyacrylate. Attempts to derivatize the acid groups in the presence of the salt, however, did not proceed with the expected results. When pyrolyzed, the sodium form of the polyacrylic acid gave several unique products including cyclopentadiene that can be used to determine soluble sodium polyacrylate in environmental samples. This paper presents the conditions for the determination of sodium polyacrylate and supporting Py–GC–mass spectrometry (MS) and Py–GC–infrared (IR) spectroscopy data to confirm the identity of the observed pyrolysis products. Literature reference to the formation of cyclopentadiene as a product from pyrolysis of polyacetylene [2] and other references [3–20] were used to propose mechanisms for the formation of the observed pyrolysis products.

## 2. Experimental

### 2.1. Sample preparation

Linear polyacrylic acid (weight-average molecular mass, $M_w \approx 243\,000$ and 0% neutralization)

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was obtained from Scientific Polymer Products, Ontario, NY, USA. Sodium polyacrylate was prepared at different levels of neutralization by adding known amounts of sodium hydroxide to water solutions of this polyacrylic acid. The water was then removed by freeze drying, and the solid polymer was placed in a quartz tube for Py–GC analysis. Methyl esters of the sodium polyacrylate were prepared as described in a previous paper [1] using Methyl-8 derivatizing reagent (Pierce, Rockford, IL, USA). The methyl esters were prepared by adding 250 $\mu$l of Methyl-8 (dimethylformamide solution of dimethyl acetal) to the dried sample. The sample was heated at 160°C for 16 h after which residual solvent was evaporated with a heat lamp and a nitrogen purge. The residue was then dissolved in 0.5 ml of methanol and analyzed by Py–GC. The sample could then be quantitated using the resulting methyl acrylate peak.

## 2.2. Pyrolysis–gas chromatography

Samples of sodium polyacrylate and methylated sodium polyacrylate solids were weighed into quartz tubes and equilibrated 5 min in a 200°C interface connected to the injection port of an HP5890 gas chromatograph equipped with flame ionization detection (FID). Samples were pyrolyzed (CDS 120 Pyroprobe Pt coil) at a set temperature of 700°C with the maximum heating rate and a 20-s interval. The pyrolysis products were split in the 220°C injection port, separated on a fused-silica capillary column (J & W DBWAX, 60 m × 0.25 mm I.D., 0.25-$\mu$m film) using a linear temperature program (50°C for 4 min then 6°C/min ramp to 220°C and a 16-min hold), and detected by FID.

## 2.3. Py–GC–MS

A 300-$\mu$g portion of 60% neutralized polyacrylic acid was weighed into a quartz boat and equilibrated 10 min in a 215°C interface connected to the injection port of a VG TRIO-1 GC–MS system. The sample was pyrolyzed at a set temperature of 700°C (CDS Pyroprobe Pt coil) with a ramp of 20°C per ms and a pyrolysis interval of 20 s. Using splitless injection through

Table 1
Infrared spectrometer conditions

| | |
|---|---|
| Transfer line temperature (°C) | 200 |
| Background scans | 100 |
| Sample scans | 100 |
| Nominal resolution (cm$^{-1}$) | 4 |
| Detector | MCT[a] |
| Apodization function | Triangular |
| Iris | 0 |
| Zerofill | 1 × |

[a] MCT = Mercury cadmium telluride.

a 220°C injection port, pyrolysis products were separated on a 60-m fused-silica capillary column (J & W DBWAX; 0.2-$\mu$m film) programmed from 40°C/4 min to 220°C at 6°C/min. Electron impact mass spectra were obtained every second over the range of 29–350 u with the detector multiplier at 330 V, a scanning electron current of 150 $\mu$A, a source temperature of 180°C, and the transfer line between the gas chromatograph and the mass spectrometer set at 200°C.

## 2.4. Py–GC–IR

Approximately 0.40 mg of sample was weighed into a quartz tube and pyrolyzed in a helium atmosphere using a CDS Pyroprobe Pt coil. The pyrolysis products were separated using a Hewlett-Packard 5890 gas chromatograph, fitted with a 60-m fused-silica capillary column (J & W DBWAX, 0.2-$\mu$m film), interfaced with a Mattson Instruments Cryolect 4800 matrix isolation IR detector. Pyrolysis and chromatographic conditions for the Py–GC–IR experiment were the same as those previously described for the Py–GC–MS experiment. The spectrophotometer conditions used to obtain the IR spectra of the isolated pyrolysis products are shown in Table 1.

## 3. Results and discussion

### 3.1. Pyrolysis experiments and identification of pyrolysis products

Fig. 1 compares pyrograms (FID) of derivatized sodium polyacrylate at different levels of neutralization. The arrow designates the reten-
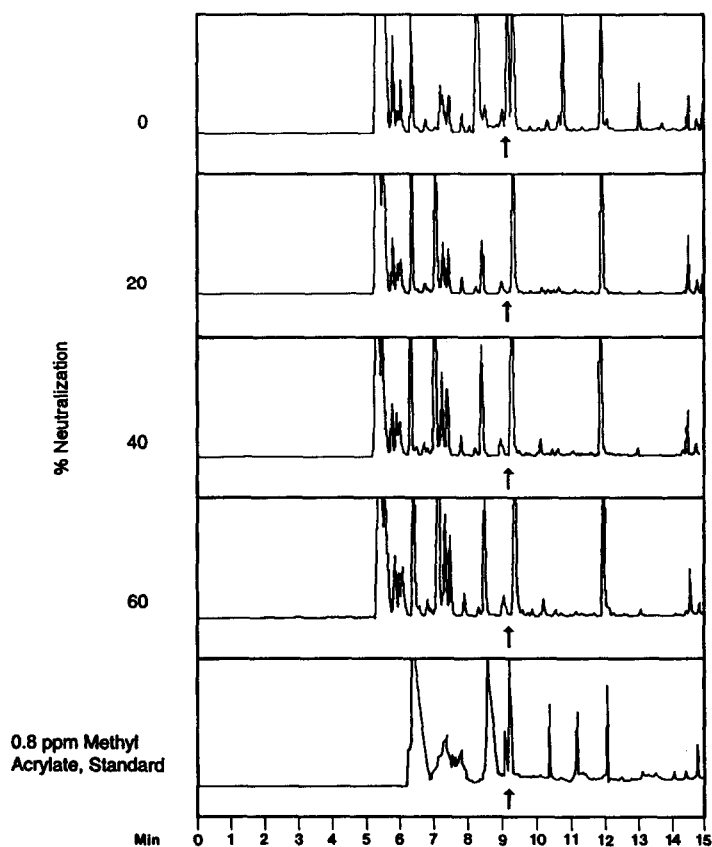
Fig. 1. Derivatization Py–GC of sodium polyacrylate at different levels of neutralization.

tion time for the methyl acrylate product from pyrolysis of polyacrylic acid (no neutralization). This peak is noticeably absent in the pyrograms of the sodium polyacrylate at higher levels of neutralization.

Pyrograms of underivatized sodium polyacrylates at different levels of neutralization are compared in Fig. 2. The peak identified as cyclopentadiene, distinctly absent in the pyrogram of un-neutralized polyacrylic acid, is present in all of the other pyrograms regardless of the level of neutralization. Note that the intensity of the other peaks decreases with increased level of neutralization. As shown in Fig. 3, this peak for cyclopentadiene is present in pyrograms of a 60% neutralized polymer with or without derivatization. Absence of this peak in the pyrogram of un-neutralized, un-derivatized polymer mixed with 60% NaCl indicates that the mecha-

nism for formation of this pyrolysis product is related to the neutralization process and not just the presence of ionic sodium.

The Py–GC–MS experiment was used to verify the identification of cyclopentadiene as a major product from pyrolysis of 60% neutralized polyacrylic acid. Fig. 4 shows the total ion current pyrogram from a 60% neutralized polyacrylic acid sample.

Peak assignments based on the mass spectral data are summarized in Table 2. Fig. 5 represents the mass spectrum of the pyrolysis product peak at scan 339 and this spectrum matches NBS Library reference spectra for cyclopentadiene.

Pyrolysis–GC–IR was subsequently used to verify the identification of cyclopentadiene as a primary product from 700°C pyrolysis of 60% neutralized polyacrylic acid. The phase-sensitive IR reconstructed chromatogram for products
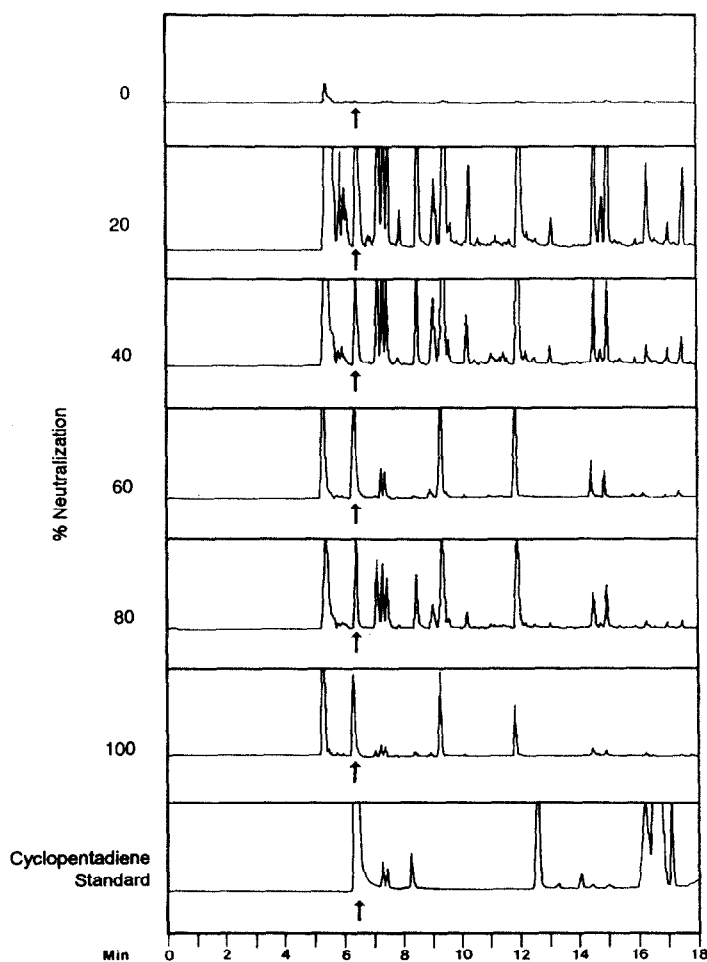
Fig. 2. Underivatized Py–GC of sodium polyacrylate at different levels of neutralization.

from pyrolysis of that sample is shown in Fig. 6 while the IR spectrum of the peak eluting at about 5.53 min is shown in Fig. 7. The major compounds present in this spectrum are methane and carbon dioxide. An expanded spectrum of the peak eluting at 5.53 min is shown in Fig. 8. This expanded spectrum strongly suggests the presence of ethane and ethene as minor components eluting alone with the carbon dioxide and methane. In addition there is evidence for vinyl twisting and wagging vibrations which suggests the possible presence of propene.

The IR spectrum of the material eluting at about 6.53 min is shown in Fig. 9. This spectrum is consistent with that of a standard spectrum of

1,3-cyclopentadiene, and it supports the data obtained by Py–GC–MS.

## 3.2. Mechanisms for formation of cyclopentadiene

Because of the commercial importance of acrylate polymers, the thermal degradation characteristics (thermal stability) of polyacrylic acid [3–9] and salts [10–18] have received much attention. Although the degradation of these materials has repeatedly been investigated the thermally stimulated processes which occur have not yet been fully delineated. In fact, the mode of degradation seems to be influenced by the
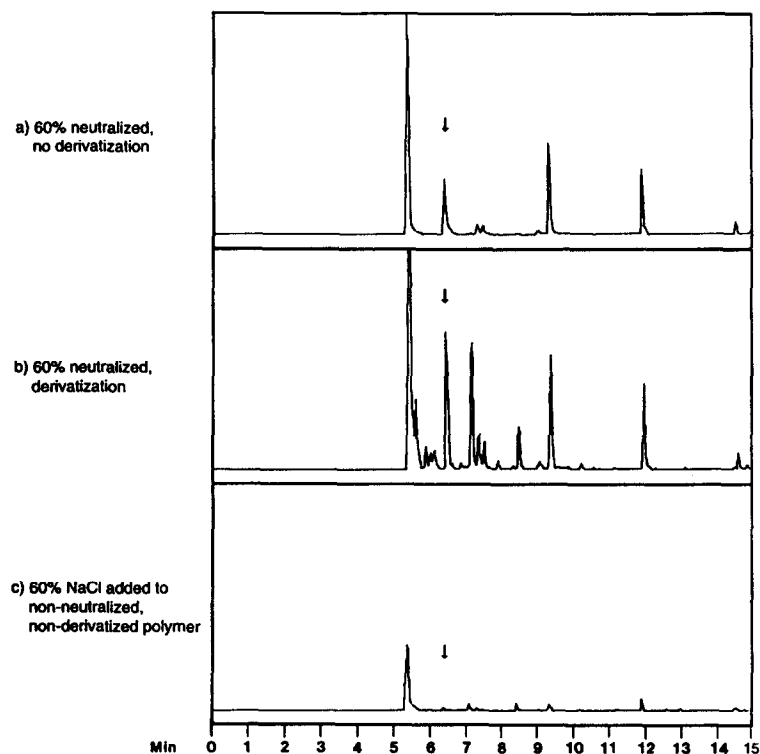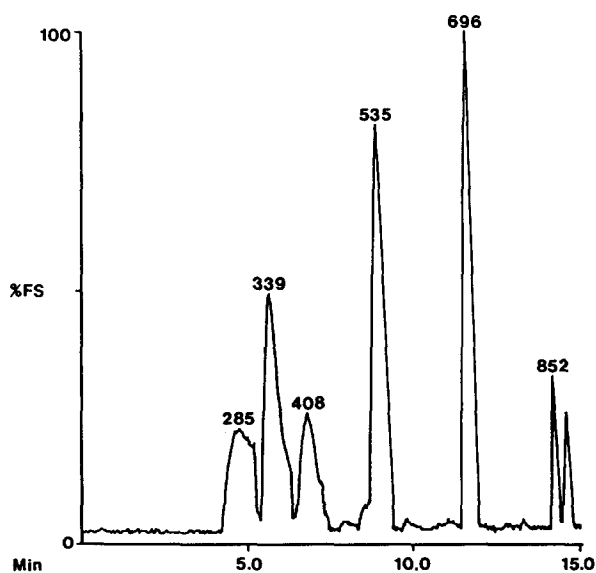
Fig. 3. Py–GC of sodium polyacrylate.



Fig. 4. GC–MS total ion current pyrogram of 60% neutralized polyacrylic acid.

means of sample preparation and the techniques used to study the decomposition. Some prominent features of the decomposition seem to be reasonably well established. The processes most often studied have been those which occur at low or moderate temperature (130–450°C) [3–18].

At approximately 150°C polyacrylic acid undergoes dehydration to form anhydrides [3–9]. Under most conditions anhydride formation is an intramolecular process to form a six-membered cyclic anhydride [7–9]. However, under film-forming conditions substantial intermolecular anhydride formation apparently occurs [10–14]. The nature of the anhydride formed may be influenced by the temperature at which the dehydration occurs [4]. At somewhat higher temperature (250–300°C), the anhydrides undergo decarboxylation to form keto structures [8–10]. The nature of the ketone formed is dependent upon the anhydride from which it originates. Initial intramolecular anhydride formation leads to the generation of cyclobutanone-type

Table 2
Mass spectra of products from pyrolysis of 60% neutralized polyacrylic acid

| Scan | Retention time (min) | Prominent $m/z$ [a] | Assignment |
|------|----------------------|----------------------|------------|
| 285 | 4.75 | (44) | Carbon dioxide |
| | | 41, 40, (42), 39 | Propylene |
| 339 | 5.65 | (66), 65, 39, 40 | 1,3-Cyclopentadiene |
| 408 | 6.80 | 79, (80), 77, 39, 51, 52 | Methyl-1,3-cyclopentadiene |
| 535 | 8.92 | (78), 77, 51, 52, 50 | Benzene |
| 696 | 11.60 | 91, (92), 65 | Toluene |
| 852 | 14.20 | 91, (106), 51, 65, 77 | Ethylbenzene or dimethylbenzene isomer |

[a] Ions listed in order of decreasing intensity with the parent ion in parentheses.
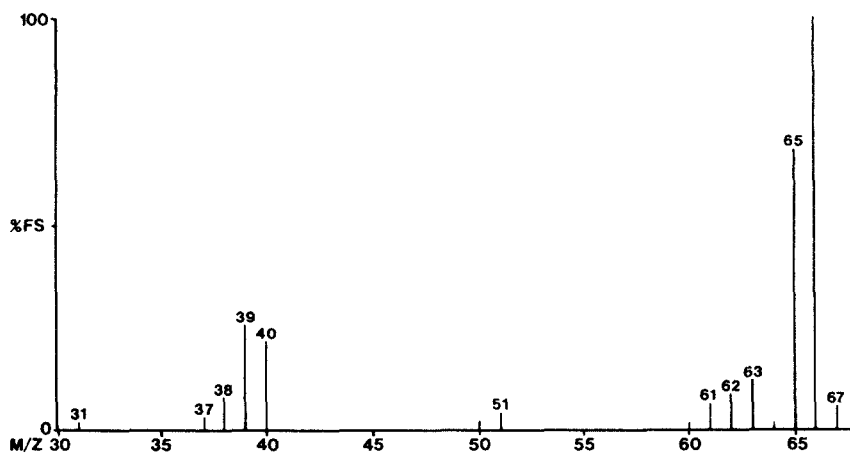


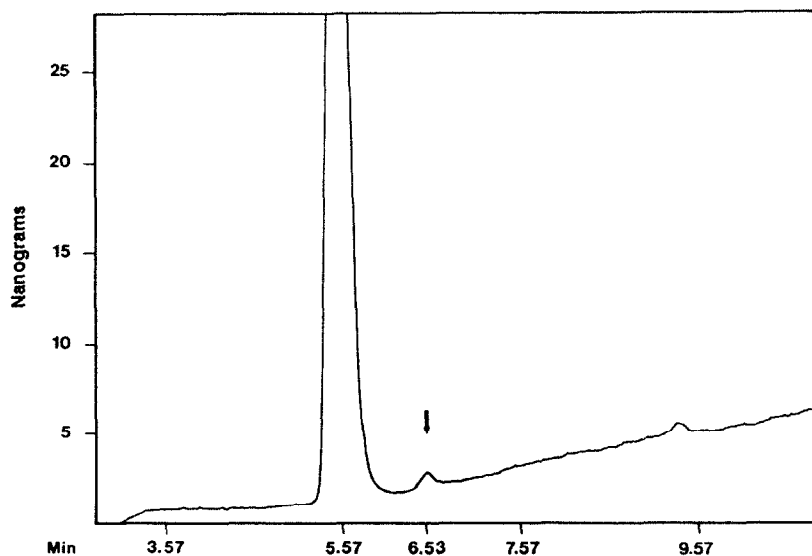Fig. 5. Mass spectrum of peak 339 (identified as 1,3-cyclopentadiene).



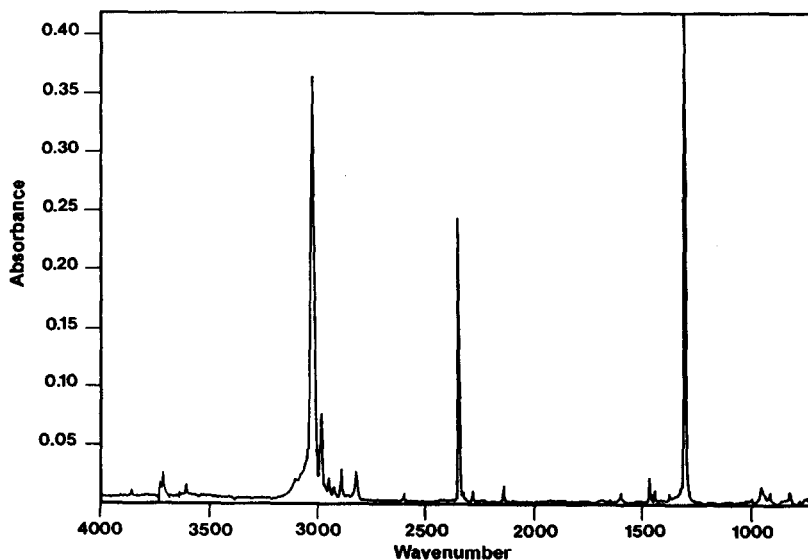Fig. 6. Phase-sensitive IR reconstructed chromatogram of 60% neutralized polyacrylic acid.

Fig. 7. IR spectrum of peak eluting at 5.53 min in Fig. 6.

structures [8,9] while intermolecular anhydride formation results in the establishment of keto cross-links [10–14] which may be utilized in the generation of superior films. Decarboxylation may be accompanied by some chain scission and ene formation [7,8,19].

Decarboxylation of cyclobutanone units within the degrading polymer may generate cyclopropyl

structures [8]. It might be anticipated that such structures would be thermally unstable and could lead to the evolution of unsaturated hydrocarbon fragments. At temperatures above 350°C significant aromatization occurs and a residual char containing phenolic functionality is formed [7].

Anhydride formation is significantly facilitated by partial neutralization of the carboxy groups of
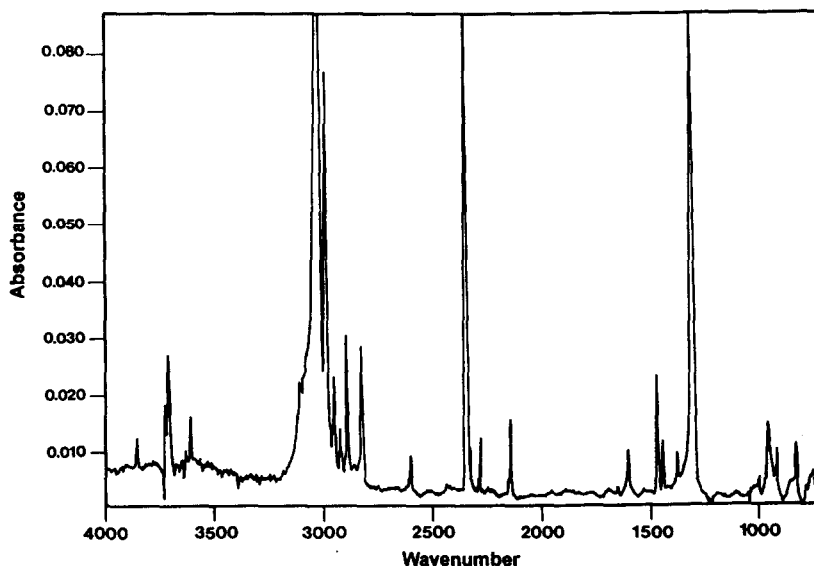


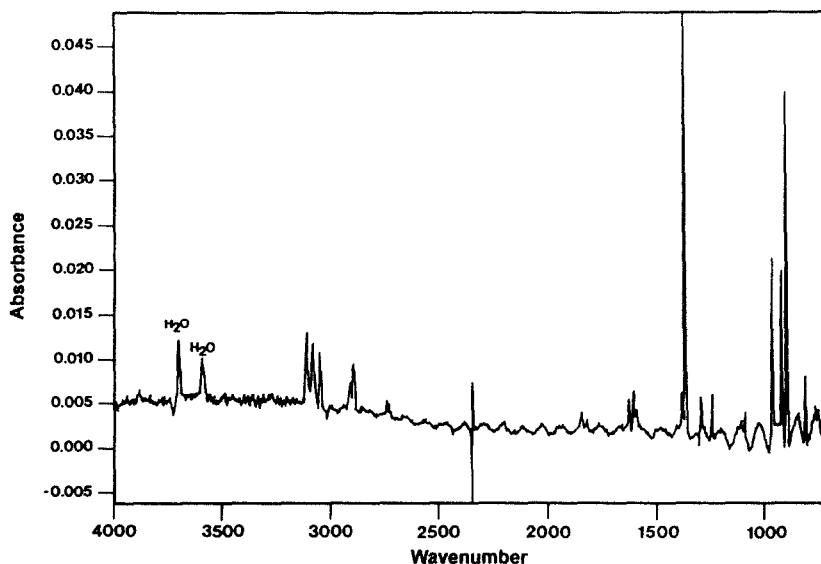Fig. 8. Enlarged IR spectrum of peak eluting at 5.53 min.

Fig. 9. IR spectrum of peak eluting at 6.53 min (identified as 1,3-cyclopentadiene).

the polyacrylic acid using an inorganic base containing a univalent cation [10,11]. This acceleration of the anhydride-forming reaction apparently arises as a consequence of decarboxylation of the carboxylate salt to form a carbanion which may attack anhydride to form a ketone and regenerate a carboxylate structure [11].

This observation has now been utilized for the development of a method of determination for polyacrylic acid as a partially neutralized salt. In this instance the acid salt was subjected to rapid thermal decomposition at 700°C, a temperature considerably greater than those (120–450°C) used for most previous studies. Under these conditions the partial salt undergoes smooth decomposition to generate a variety of small molecule fragments including most prominently 1,3-cyclopentadiene. As noted above, it is the formation of cyclopentadiene which serves as the basis for the determination method described. As shown in Fig. 10, the presence of even a small amount of neutralization in the starting poly(acid) may greatly accelerate the decarboxylation of the anhydride formed in the initial dehydration step.

As previously noted [10], the carboxylate undergoes decarboxylation to generate a main-chain carbanion. This carbanion is strongly nucleophilic and may attack a neighboring anhydride unit. Nucleophilic addition followed by elimination generates a cyclobutanone unit and at the same time exposes another carboxylate group which is as reactive as the first leading to a
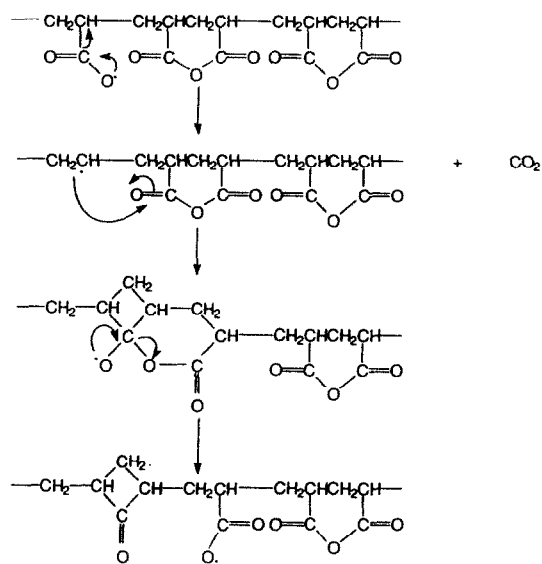


Fig. 10. Decomposition of the anhydride formed from dehydration of partially neutralized polyacrylic acid.

repetition of the sequence: decarboxylation, cyclobutanone formation, generation of another carboxylate unit. This decarboxylation assisted by a neighboring carboxylate group moves rapidly along the polymer chain and accounts for the rapid evolution of carbon dioxide. Since a carboxylate group is regenerated in the ketone-forming step this process should be promoted by even small levels of neutralization. This was demonstrated experimentally in that polyacrylic acid neutralized to the extent of 0.5 to 50% exhibits the same pyrolysis behavior. A possible mode of fragmentation of the keto structure formed from decarboxylation of the anhydride is displayed in Fig. 11.

Of course other less prominent processes are occurring simultaneously with cyclopentadiene formation. A variety of small molecule fragments are formed. It is likely that some of this

reflects polyene formation. An alternative mode of formation of cyclopentadiene would be the cyclization/fragmentation of polyene [20].

## 4. Conclusions

Pyrolysis of sodium polyacrylate at 700°C produced 1,3-cyclopentadiene as a unique degradation product and mechanisms were presented for the formation of this compound. The pyrolysis yield of 1,3-cyclopentadiene appeared to be independent of the level of neutralization although yields of other pyrolysis products decreased with increasing levels of neutralization. Although not fully developed in this study, this unique pyrolysis mechanism could be the basis for quantitative procedures to determine sodium polyacrylate in environmental samples. Additional validation is warranted to determine the quantitative limits of this pyrolysis procedure.
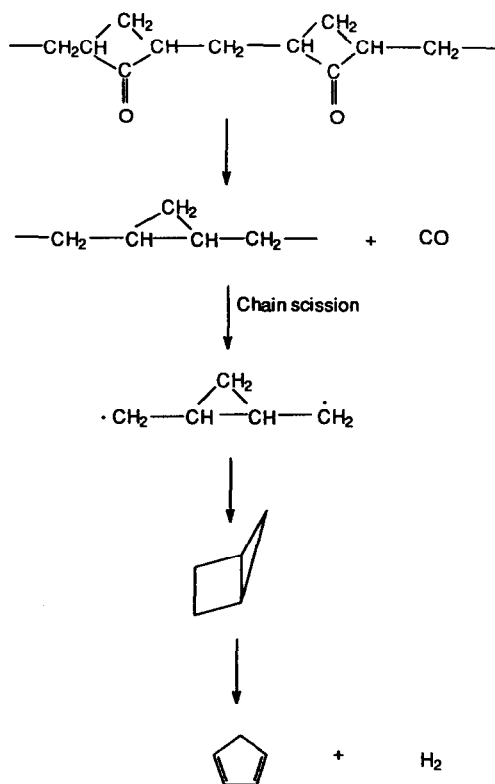


Fig. 11. Potential fragmentation mode leading to the formation of 1,3-cyclopentadiene.

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