

Thermal behavior of 1,3-butadiene-acrylic acid copolymers

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SUMMARY

Thermal behavior studies were carried out on copolymer fractions of 1,3-butadiene-acrylic acid (Bu/AA) obtained from bulk polymerization. Three procedures were used: a) Decomposition temperature, b) A combined method: thermal and electron impact degradation, c) Differential scanning calorimetry (D.S.C.). Thus, limiting stability temperatures and the different products could be determined. A behavior of Bu/AA after addition of different chemicals with suppressor effects on the thermal decomposition has also been studied. The resulting products, analyzed after thermal decomposition, showed that the retardation occurred in different ways depending on the inhibitor used.

INTRODUCTION

The thermal stability of polymers, particularly their degradation behavior, helps to reveal their structures, such as the sequence and arrangement of the different monomers and functional groups, and possible cross-links. The kinetics of depolymerization and the effects of different variables on degradation products, such as pressure, temperature, time, additives etc. has also been studied(1).

Since organic polymers are molecularly degraded and burn in a flame, fire retardants have been developed(2). There is substantial literature on the addition of retardants to polymers such as cellulose(3), acrylonitrile, acrylic fibers, polybutadiene rubber(4), etc. This interest in the use of flame retardants is due to the different behavior of each polymer towards the flame. It is necessary to develop a specific retardant for each of them. Several methods have been used to characterize the thermal degradation. Some authors used combined methods such as pyrolysis with gas chromatography and mass spectrometry(5), i.e., methods which allow to identify some of the decomposition products upon pyrolytic degradation. Other authors support their results with synthetic methods and conditions of thermal stability changes(6).

The present paper deals with the thermal stability of purified Bu/AA fractions using a combination of experimental methods which indicates the stability of the polymer as a function of temperature, the nature of the

degradation products in the presence and absence of fire retardants and finally, their ignition temperatures.

EXPERIMENTAL

Synthesis of 1,3-butadiene-acrylic acid copolymer(Bu/AA): The copolymer was obtained by a bulk polymerization method at 70°C using benzoyl peroxide initiator at 1% wt/wt(7). The polymer was a liquid (Mn: 3720 by V.P.O.) with a carboxyl content of 0.45 eq/100g and intrinsic viscosity 0.098 dl/g in C_6H_6 at 25°C.

Purification by fractional precipitation: 7g Bu/AA were dissolved in 4ml benzene, using 14ml acetone as nonsolvent. It was kept at 5°C for 3 hs and then centrifuged 20' at 2000rpm. The resulting precipitate (F_1) was washed with tetrahydrofuran and dried at reduced pressure and room temperature. Then, to the upper layer were added 40ml methanol and it was kept at 5°C for 24 hs. The resulting precipitate (F_2) was obtained by the same procedure followed for (F_1). From the upper layer, F_3 was obtained after evaporation and dried at reduced pressure. This procedure proved the presence of a copolymer rather than a mixture of homopolymers.

Purification by gel permeation chromatography(GPC): F_2 obtained by fractional precipitation was analyzed by GPC. Using a $25 \times 1,5$ cm glass column filled with Sephadex LH-20 at 60 ml/h at a constant flow and a constant pressure due to a column with solvent of 100 cm height, 0.1 g of F_2 were chromatographed after dissolving it in tetrahydrofuran and the same solvent used as eluent.

Thermal decomposition studies:
The equipment consisted of a "50035 Lindberg Heavy Duty Mini Mite" furnace equipped with an internal thermocouple; a reactor containing an aluminium pan where the sample was placed. The sample consisted of purified copolymer and copolymer plus retardants. Four different systems were prepared with the copolymer containing 11,5% chlorinated paraffin (ClP) : 9% chlorinated paraffin along with 2,5% of monoammonium phosphate (MAP) : 9% bromocyclopentane(BrC) along with 2,5% of monoammonium phosphate and 11,5% bromocyclopentane. At the end of the reactor a trap was placed to collect the liquid products and a manometer(Figure 1). The whole apparatus was of Pyrex glass.
Sample quantity: 150mg.
Pressure: 3×10^{-3} mm Hg.
Heating time: 3hs.
Temperatures: 300° and 400°C.

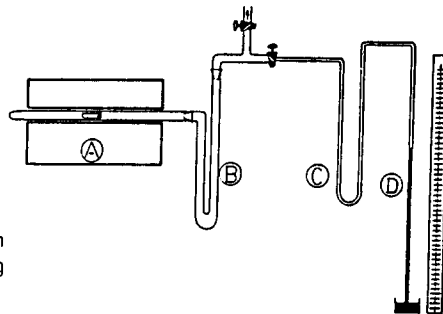


Figure 1: Schematic representation of the equipment used for research of the thermal decomposition of 1,3 Bu/AA copolymer. A)Furnace; B)Trap for liquid and gaseous products; C)Trap for gaseous products; D)Manometer

Combined methods: thermal degradation and electron-impact. A 3300 Finnigan mass spectrometer attached to a system of INCOS data from the Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, was used. A modification was made related to the introduction and ionization of the

sample involving a temperature regulator fitted in the injection zone. This method allowed us to perform the thermal degradation in the ionization chamber and as the different fragments formed, they were immediately analyzed. Thus different spectra at different temperatures were obtained. The temperature program ranged from 300° to 400°C.

Differential scanning calorimetry (DSC) was performed in a 990 Du Pont differential scanning calorimeter between room temperature and 250°C with a heating program of 10°C/min. Ten mg of sample were used and placed into a round aluminium sample pan. The reference pan contained anhydrous alumina which is stable at this temperature range. In order to avoid gas evolution, nitrogen at a pressure of 9.5 atm. was used.

Determination of ignition points: The experiments were done in a self-designed equipment. It consisted of a thermostat with variable temperatures between 20 and 600°C, non-automatic handling, a porcelain capsule with a silica bath and micro-flame. The sample was placed into the porcelain capsule with a micro-flame over it. It was heated by using a temperature regulator at a constant rate. With the first flammable gases a flame appeared and when the concentration of the flammable products was sufficient the sample reached complete combustion.

RESULTS AND DISCUSSION

To determine thermal decomposition, experiments were carried out at 300° and 400°C. These temperatures were chosen according to thermogram runs which showed that the copolymer lost 36% weight at 300°C and 100% at 400°C.

The products identified at 300°C were: liquid (34,8%), gaseous (1,2%) and solid residues (64%).

The products identified at 400°C were: liquid products A and B with different volatility (98,4%) and gaseous product (1,6%).

The liquid products were analyzed by infrared spectroscopy and thin layer chromatography. Derivatives obtained by reaction with diazomethane were analyzed by mass spectrometry.

The infrared products showed resonance bands common to all liquid products.

Signal (μm)	Group
3,5	C-H
5,7	C=O
6,9	CH ₂
10,5	H-C=C-H (trans)
14,2	H-C=C-H (cis)

The chromatographic layers were sprayed with bromophenol blue (specific indicator for carboxylic acids).

The liquid products were mainly mixtures of carboxylic acids with molecular weights ranging from 300 to 400 m/z by mass spectrometric analysis.

Gas chromatographic analysis of gaseous products showed a mixture of about 15 or 17 unidentified products. However, they were probably hydrocarbons owing to their neutral pH, negative reaction to bromophenol blue, to 2,4-dinitrophenyl hydrazine, and other reagents.

The analysis of the solid residue by infrared spectroscopy showed changes in the cis-trans ratio related to the original copolymer.

When a sample was heated at 160°C and was analyzed before and after

this treatment, practically no loss of weight was observed indicating the absence of volatile fractions. However, internal structural changes were mainly observed by changes in the cis-trans ratio (bands at 14,2 and 10,5 μm).

Figure 2 (DSC) shows that the polymer was stable until approximately 120°C with an exothermic maximum at 160°C. This change is probably due to crosslinking and internal rearrangements and not to evolution of gaseous products (See TD-EI).

In the combined method (TD-EI) the polymer was heated from room temperature to 400°C (Figure 3). At 160°C the ionic current was very low whereas at 250°C it reached a maximum and remained at the same intensity until 400°C. This may indicate that degradation with evolution of volatile fractions started only at 250°C. The m/z values for these volatile fractions ranged from 2 to 1000; values above 1000 could not be observed due to equipment limitations.

The volatile liquid fractions of the thermolysis at 300°C were also analyzed by the combined method (TD-EI). The ionic current for hydrogen (m/z : 2) increased from room temperature up to 100% (indicative of the ion with maximum concentration) at about 150°C. This would justify the combustion of the fractions which volatilize (Figure 4).

Once the thermal behavior of the Bu/AA copolymer was known, thermogram studies were done with the retardants mentioned in the experimental part.

Figures 5 and 6 show inhibition due to the different retardants.

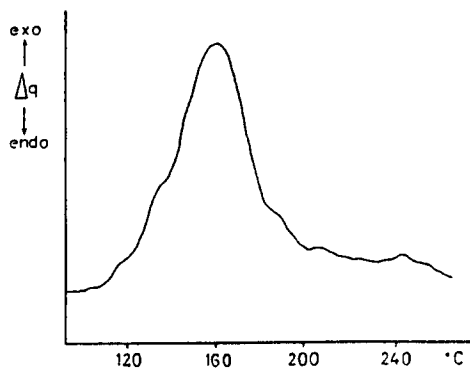


Figure 2: DSC for the 1,3-Bu-tadiene-Acrylic Acid copolymer.

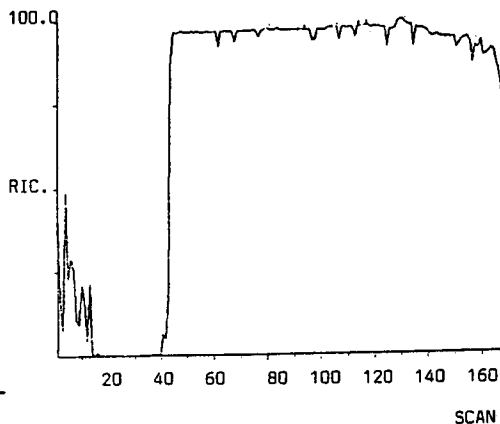
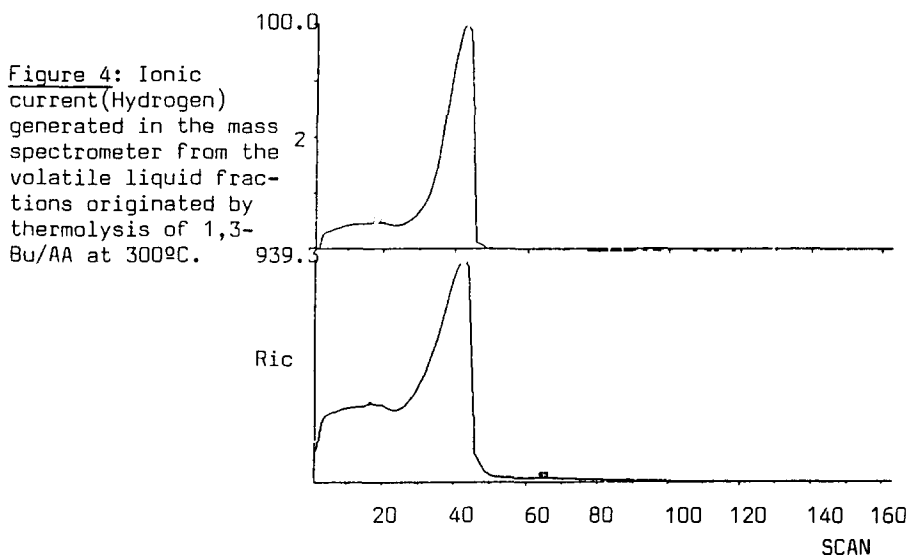


Figure 3: Ionic current generated in the mass spectrometer and by heating of 1,3 Bu/AA from 20° to 400°C.



Mass spectrometric analysis show that when chlorinated paraffin (ClP) was used, chlorinated compounds, which are less volatile due to the increase in the molecular weight and almost self extinguishable due to the inhibition effect of chlorine, are obtained by thermal decomposition. This may indicate that ClP inhibited only at a gaseous level.

A direct relationship exists between combustion efficiency and volatility of the fractions obtained by thermolysis.

A synergistic action was observed when both monoammonium phosphate (MAP) and ClP were used probably because the combined use of phosphorus and chlorine reduce the formation of liquid products.

When bromocyclopentane was added, a diminution in the formation of gaseous products was observed but it was not as effective as ClP.

The BrC and MAP system showed a decrease in the formation of liquid and gaseous products. The most efficient of these systems was that contained BrC plus MAP.

In comparative analysis of the ignition points at 180°C an evolution of flammable gases (flame) was observed for Bu/AA maintained up to 250°C. From here up to 580°C degradation and elimination of non-combustible gases occurred.

The mixture containing Bu/AA and ClP showed first an evolution of non-flammable gases and between 260 and 320°C an elimination of flammable gases. Then (up to 580°C), there was decomposition without flame.

As regards Bu/AA-BrC mixture, non-flammable gases evolved from 350°C and ignition occurred at 500°C.

In the Bu/AA-BrC- MAP mixture gas evolution occurred from 260°C; combustion did not occur up to 580°C.

Figure 5: Inhibition of different chemicals on the thermal decomposition of 1,3-Bu/AA copolymer at 300°C
 --- Residue, --- Liquid products, --- Gaseous products.

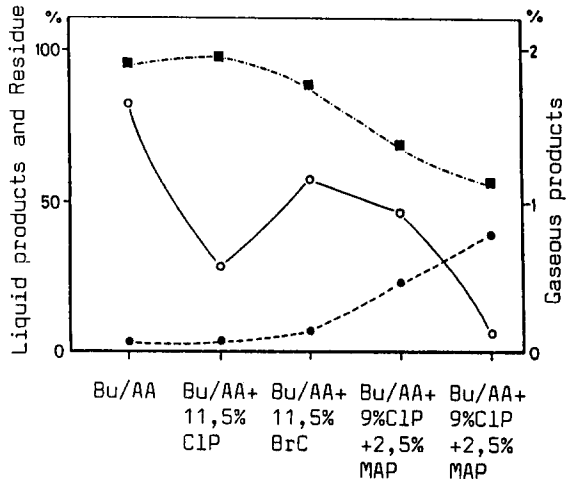
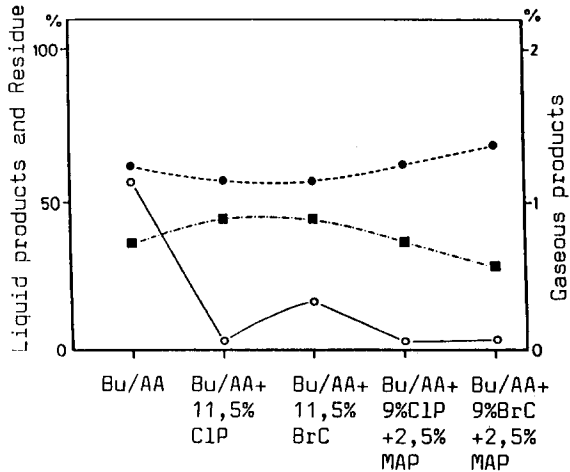


Figure 6: Inhibition of different chemicals on the thermal decomposition of 1,3-Bu/AA copolymer at 400°C
 --- Residue, --- Liquid products, --- Gaseous products.



CONCLUSIONS

The Bu/AA copolymer is stable up to about 120°C; beyond this temperature level and at different temperatures it undergoes successively internal rearrangement, decomposition with evolution of volatile fractions and formation of carbon residues in some cases. The decomposition products were

classified into hydrocarbons for the gaseous fractions and carboxylated compounds of low molecular weight for the liquid fractions.

When chlorinated inhibitors were present, the liquid decomposition products also contained halogens, therefore they were less combustible.

In general, the inhibitors showed good results in the thermal degradation of Bu/AA copolymer. Inhibition took place in the gaseous phase and in others, in the solid phase. The maximum inhibition was obtained with the use of bromocyclopentane (BrC) plus monoammonium phosphate (MAP).

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