Thermal Properties of Copolymers of 2-Acrylamido-2-methylpropanesulphonic Acid with Some Vinyl Monomers

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SUMMARY: 2-Acrylamido-2-methylpropanesulphonic acid (AMPS) was copolymerized with both acrylic acid (AA) and vinyl acetate (VA) at different compositions. The thermal behaviors of the resulted copolymers, PAMPS, PAA and PVA were studied using thermogravimetric analyses. In all cases of homopolymers and copolymers, there are two degradation stages. The observed enhancement of the thermal properties of the copolymers compared with that of PAMPS are attributed to intramolecular cyclization reactions and ring formations. The apparent activation energies of the decomposition were determined and correlated to the sequence of the thermal stabilities of the various polymers.

I. INTRODUCTION

The advent of new technologies and the search for material with new properties has promoted the synthesis of a wide range of copolymers in the last few decades [1-3]. Detailed mechanistic treatment in terms of individual reaction steps of the thermal degradation are difficult, but the free radical theory has nevertheless allowed a kinetic treatment of these processes, and the phenomenological approach provided by thermogravimetry (TG) and allied methods has been very useful in this respect [4-6].

In practice, it is often observed that thermal decomposition pathways which occur in the polymers depend largely upon the nature of the functional group present, and identification of the thermal fragmentation products is often a difficult task. Thermal stability and mechanism of thermal decomposition are related, but such a relationship is often complicated by the effects of several overlapping factors [7-8]. In most cases, the thermal stability depends upon the availability of hydrogen atoms along the polymer chain or other thermal decomposition mechanisms at higher temperature.

In this paper the thermal behavior of the copolymers of AMPS with acrylic acid and vinyl acetate will be dealt together with the corresponding homopolymers. A range of different copolymers covering the entire composition range between PAMPS and a corresponding PAA or PVA have been prepared and there thermal degradation and stability have been studied.

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2. EXPERIMENTAL

2.1 Materials

Acrylic acid (AA) (BDH) was dried over $CaCl_2$ and kept below 0^oC. Vinyl acetate (VA) (Merck grade) was dried over $CaCl_2$ and distilled at 73^oC. AMPS (Merck grade) was recrystallized from hot ethanol. Ammonium persulphate (APS) (Sigma) was recrystallized from deionized water. The other chemical reagents and solvents were of analytical pure grade and used without further purification.

2.2 Copolymers preparation and characterization

Homopolymers of AA, VA and AMPS, and copolymers of AMPS – AA and AMPS-VA were prepared by free radical initiation using ammonium persulphate as initiator in deionized water as solvent and at $60C^o$, to about 10% conversion. The polymers were then precipitated in acetone, filtered off and dried at $40C^o$ for several hours. Five different compositions of the copolymers were prepared having the compositions of 25, 33, 50, 66, and 75 mol% of AA or VA units.

Elemental analysis for sulfur was conducted by Microanalytical Units of Cairo University. The average of five values of sulfur contents obtained for each sample was used for the determination of the copolymer composition [9]. IR spectra was obtained using a Perkin-Elmer 883 Spectrophotometer, the samples were examined as thin film cast on sodium chloride plates [9].

2.3 Thermal Methods of Analysis

Thermal gravimetric analysis (TG), and derivative thermogravimetric analysis (DTG) were performed using a Shimadzu TGA-50H module. The thermal analyses were carried out from ambient temperature to 700 ^0C, at a heating rate of $10^0C\ min^{-1}$. The initial rates of the degradation of homopolymers, and the resulted polymers, were determined by means of TG at different intervals. The activation energies of the decomposition were obtained by application of the Arrhenius equation.

3. RESULTS AND DISUSSION

3.1 Thermal degradation of AMPS-AA copolymers.

The thermal degradation of acrylic acid is well known in literature [10-11]. It degrades in two steps as shown in Fig. 1.

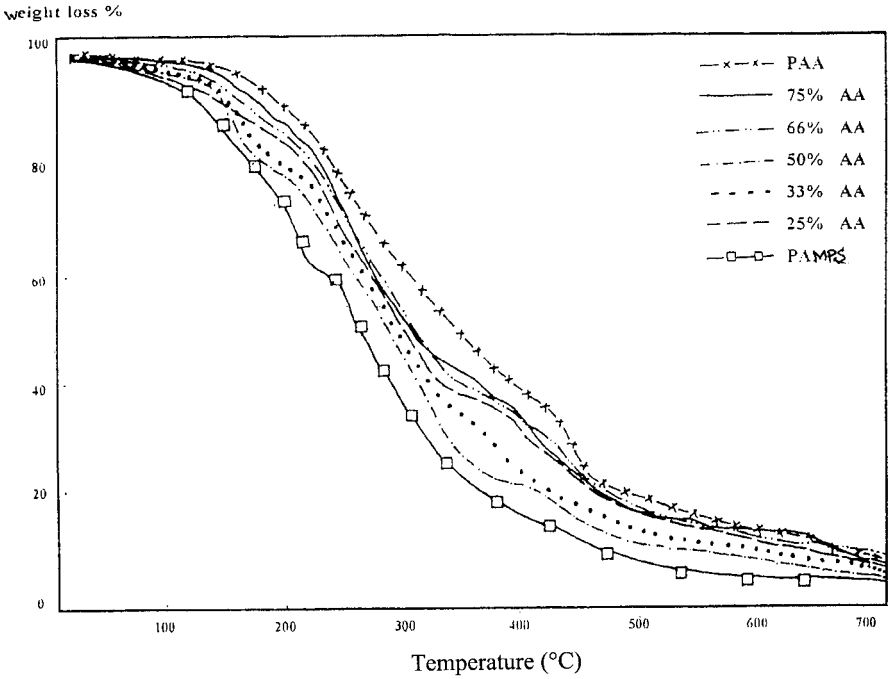
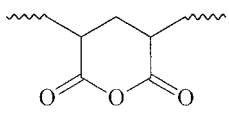


Figure 1. TGA curve of PAMPS, PAA homopolymers and AMPS-AA copolymers

If the temperature is gradually raised PAA begin to degrade at about 180°C. The polymer residue after initial product evolution degrade slowly until about 430°C, at which point extensive breakdown occurs leaving a small amount of carboneous residue. It has been reported that the first stage of breakdown is due mainly to intramolecular dehydration to produce six membered anhydride rings in the polymer backbone [12-14] as shown in Scheme (I).



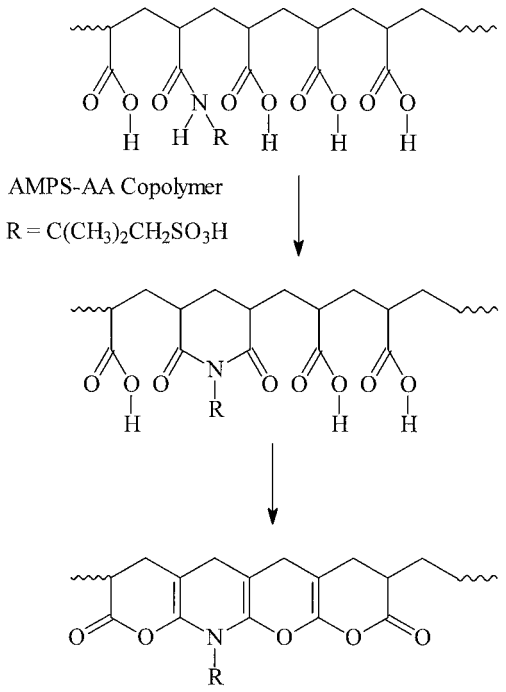
Scheme I

The high temperature decomposition involves fragmentation of the modified chain structure to give a complex mixture of products. The gaseous products at this stage include CO, CO_2,

CH_4, and traces of alkenes [15-16]. The degradation of PAMPS was previously discussed in our laboratory [17].

On the other hand the AMPS-AA copolymers exhibit two degradating stages, and their stabilities are in between that of the PAA and PAMPS homopolymer as indicated in Fig.1.

The first stage of degradation starts at temperature range 120°C to 175°C and ends at temperature range 350°C to 420°C. The thermal degradation of this stage involves the formation of 6-membered anhydrides rings due to the reaction of adjacent acid groups and to intramolecular cyclization between AMPS and AA units as suggested in Scheme (II).



Scheme II

As the degradation continues, there appear to be loss of hydrogen from the backbone of the polymer and also a gradual loss of carbonyl groups. At higher temperature, there is formation of a highly aromatic chear that possesses a substantial number of phenol rings [14].

Table 1 represents TG data for PAMPS, PAA and AMPS-AA copolymers at various copolymers.

Table 1. TG data for PAA, PAMPS and AMPS-AA polymers

Polymer AA Mol %	First Stage		Second stage	
	T_{max} °C	Wt loss %	T_{max} °C	Wt loss %
0 (PAMPS)	240	35	355	70
25	300	52	450	86
33	310	50	470	85
50	315	48	480	84
66	320	47	490	83
75	325	46	500	88
100 (PAA)	350	45	520	80

3.2 Degradation rate constants and the activation energies of AMPS-AA copolymer

The degradation rate constants of the PAMPS, PAA and AMPS-AA copolymers were determined from TG curves at the initial stages of decomposition, by correlations of weight loss % as function of time at different temperatures. The activation energies were determined using Arrhenius equation as represented in Fig. 2.

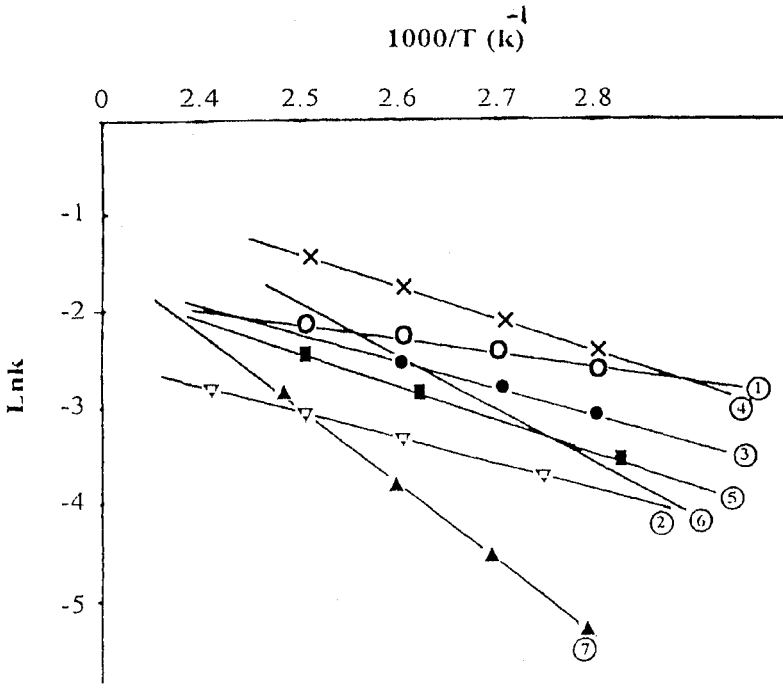


Figure 2. Arrhenius plots the rate constants of degradation of: (1) PAMPS; (2) 25% PAA; (3) 33% PAA; (4) 50% PAA; (5) 66% PAA; (6) 75% PAA; (7) PAA.

Table 2 lists the effective activation energies of different copolymers. The activation energies are in the same sequence as the stabilities of homopolymers and copolymers.

Table 2. Activation energies of the thermal degradation of PAMPS, PAA and AMPS-AA polymers.

Polymers (AA mol %)	Ea (kJ/mol)
0 (PAMPS)	13.9
25	20.7
33	22.3
50	27.7
66	45.7
100 (PAA)	66.5

3.3 Thermal degradation of AMPS-VA copolymers

Fig. 3 shows the thermal degradation of PVA, PAMPS and AMPS-VA copolymers.

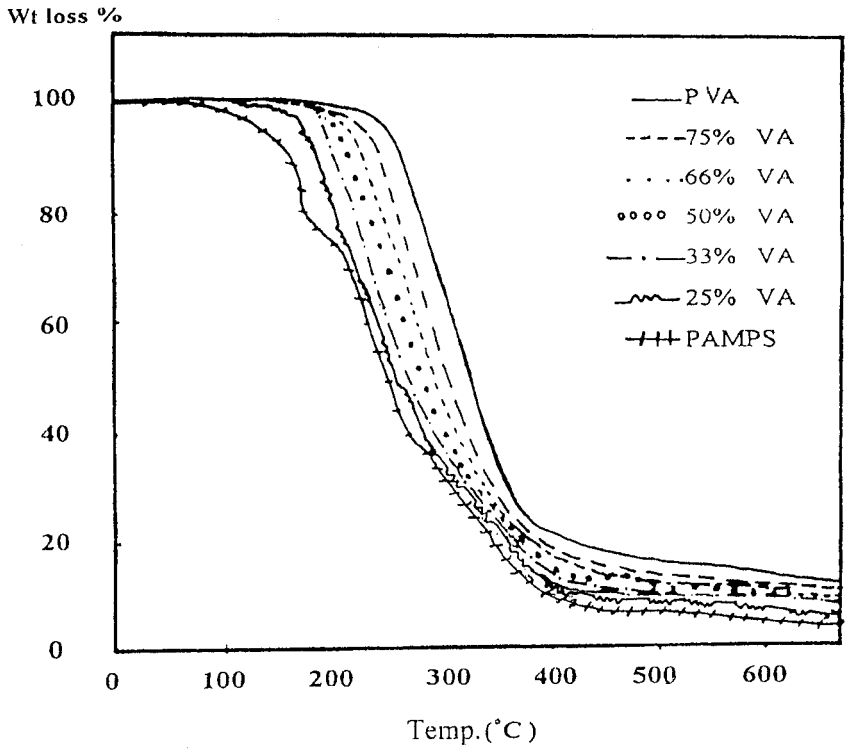
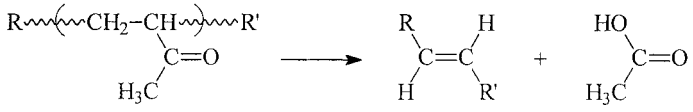


Figure 3. TGA curve of PAMP, PVA homopolymers and AMPS-VA copolymers.

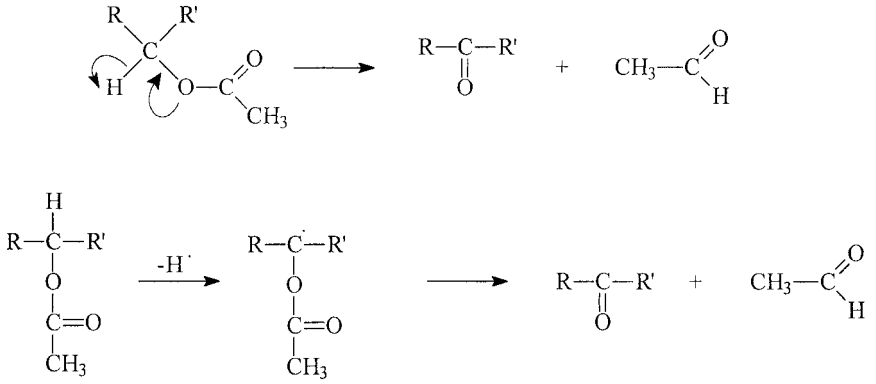
The degradation of PVA is well studied and reported [18-19]. All the curves exhibit the two stages of degradation behaviour. The earlier investigations of PVA degrades at about 230°C which are due to evolution of acetic acid [20-21] (Scheme III).



PVA

Scheme III

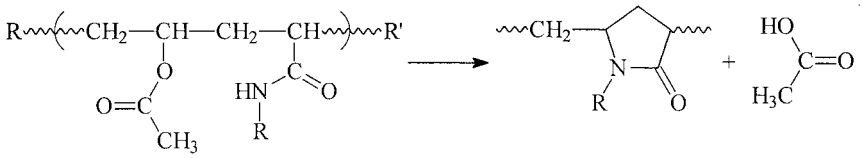
The second part of the degradation curve reveal the actual thermal stability of the polymers at the pyrolysis conditions used. Both molecular and radical mechanisms could be suggested in Scheme IV.



Scheme IV

On the other side the TG curves of AMPS-VA exhibit also two degradation stages. The first stage of breakdown starts at temperature between 190-220°C and ends at temperature between 380-420°C. The mass loss in this stage corresponds to loss of acetic and sulphonic acids. The second stage of decomposition occurs with a rate maximum near 500°C and involves fragmentation of the backbone structures. A similar results are obtained for the degradation of vinyl bromide-vinyl acetate copolymer [22].

The observed high thermal stability of AMPS-VA copolymers could be resulted from the intramolecular cyclization reaction and formation of pyrrolidone ring structure as proposed in the following Scheme (V).



R = $C(CH_3)_2CH_2SO_3H$

Scheme V

Table 3 summarizes the wt loss for each polymer and T_{max} for each stage obtained by derivative thermogravimetric method.

Table 3. TG data for PVA, PAMPS and AMPS-VA polymers.

Polymer VA Mol %	First Stage		Second stage	
	T_{max} °C	Wt loss %	T_{max} °C	Wt loss %
0 (PAMPS)	240	35	355	70
25	230	42	400	86
33	240	42	420	85
50	260	41	430	84
66	270	39	435	82
75	280	38	440	81
100 (PVA)	300	40	450	80

3.4 Degradation rate constants and the activation energies of AMPS-VA copolymers

The degradation rate constants of PVA, PAMPS homopolymer and AMPS-VA copolymers were determined as described in sections 3.2. The activation energies of decomposition of homo-and copolymers of AMPS-VA were determined from the temperature dependence of the initial rate of decomposition according to Arrhenius relationship as shown in Fig. 4.

Table 4 listed the data of activation energies corresponds with the copolymer compositions. The results show that the activation energies decrease from 43.6 to 13.9 kJ/mol as AMPS concentration in the copolymer increases, indicating that the polymers with high VA contents, enhance the thermal stability of copolymer.

As an outlook of this work and because of its importance in polymer technology, the study of their applications such as dyeability, electrical conductivity, surfactant properties, ... etc. are now taken in consideration for further investigation.

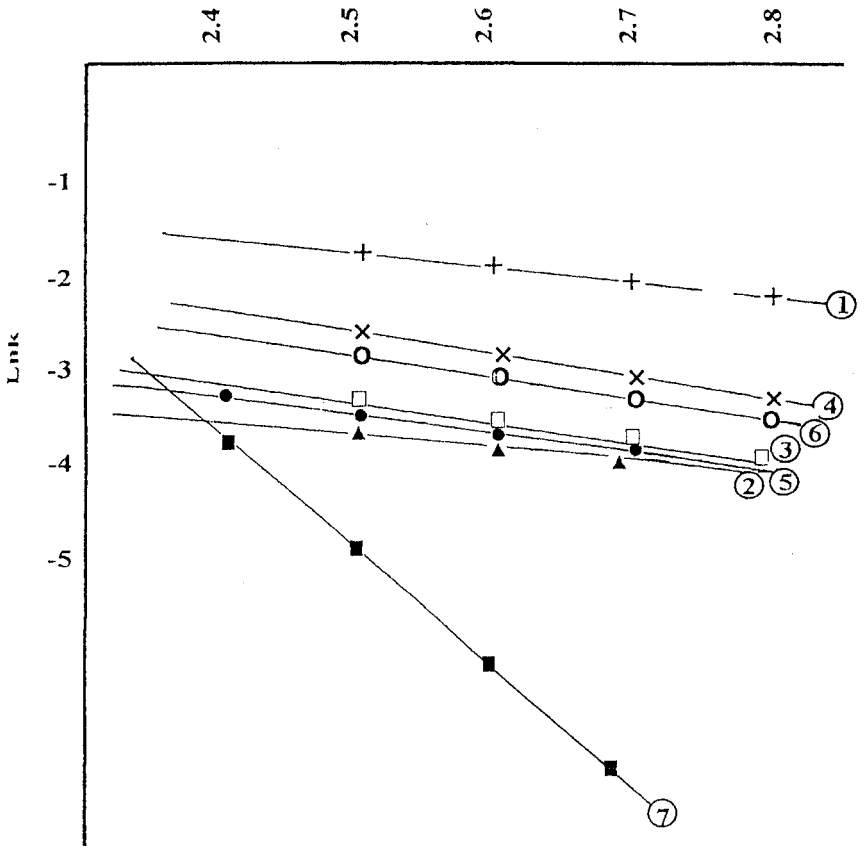


Figure 4. Arrhenius plots the rate constants of degradation of: (1) PAMPS; (2) 25% PVA; (3) 33% PVA; (4) 50% PVA; (5) 66% PVA; (6) 75% PVA; (7) PVA.

Table 4. Activation energies of the thermal degradation of PAMPS, PVA, AMPS-VA polymers.

Polymers (VA mol %)	E_a (kJ / mol)
0 (PAMPS)	13.9
25	17.9
33	16.6
50	20.7
66	21.7
75	22.0
100 (PVA)	43.6

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