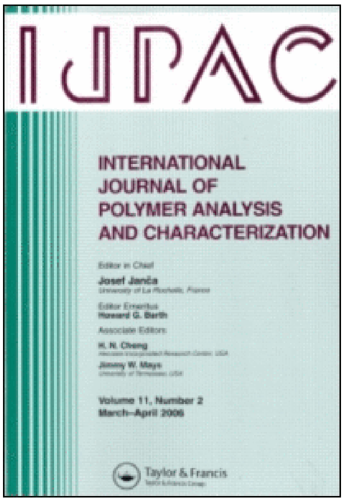

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Thermal Stability of Maleic Acid-Vinyl Acetate Copolymer in Aqueous Solution: Size Exclusion Chromatography Analysis

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Thermal Stability of Maleic Acid-Vinyl Acetate Copolymer in Aqueous Solution: Size Exclusion Chromatography Analysis

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Abstract: Sodium maleate-vinyl acetate (NaM-VA) and maleic acid-vinyl acetate (MAc-VA) copolymers were synthesized and characterized and their aqueous solutions were kept at 25 and 100°C. The molecular weight (M_W) of the copolymers was measured after different times of storage by size exclusion chromatography, and IR spectra were recorded. At 100°C, NaM-VA showed a continuous decrease of MW, which can occur due to the chain breaking and/or chemical modification, while for MAc-VA copolymer a decrease was observed, followed by an increase of the apparent MW. This difference of behavior was attributed to some interchain chemical reactions. The decrease in the molecular weight of the two copolymers at 25°C was found to be less important than at 100°C.

Keywords: Maleic anhydride copolymers; Maleic acid copolymers; SEC analysis; Polyelectrolyte solutions; Stability of polymers

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INTRODUCTION

Interest in maleic anhydride based copolymers is continually growing due to their successful applications as drugs or drug carriers,[1] supports for enzymes,[2,3] antiscale agents, phosphate substitutes in detergents, and soil conditioners.[4] All these applications involve the advanced stability of maleic anhydride copolymers before their chemical transformation (hydrolysis, neutralization, esterification, amidation) and thereafter in aqueous media.

Recently, several articles and patents have been concerned with the stability of aqueous solutions of maleic anhydride/acid-alkyl vinyl ether copolymers. Different methods or processes were proposed to obtain stable aqueous solutions, such as the addition of small quantities of ethylenediaminotetraacetic acid, inorganic salts or their mixtures, and vitamin E.[5–9]

A few studies have been performed on the stability of maleic anhydride-vinyl acetate copolymer in aqueous solution[10,11] or in dry form.[12] They reported only some chemical modifications of the polymer such as hydrolysis of anhydride cycle, deacetylation, and lactonization. Based on our previous observations, we have determined by means of size exclusion chromatography (SEC) the change in the molecular weight (MW) of the maleic acid-vinyl acetate copolymer and its Na salt during the storage of their aqueous solutions at 25 and 100°C. The storage conditions were chosen in order to follow the influence of the chemical structure and of the heating on the copolymer because some of its applications involve quite high temperatures.[13,14]

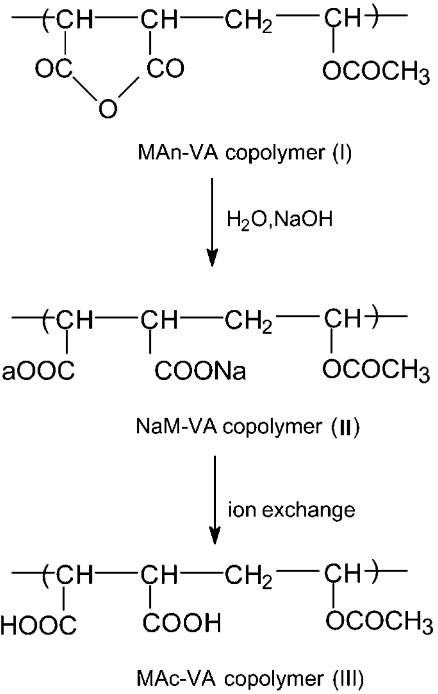
EXPERIMENTAL SECTION

Polymers

The copolymer **I** of maleic anhydride (MAn) with vinyl acetate (VA) was synthesized by radical polymerization in benzene at 80°C,[15] the monomers, the catalyst, and the solvent being carefully purified before use according to standard methods. Under these conditions, an alternating distribution of the two monomers along the chain[16] can be identified. The composition of MAn-VA copolymer was determined by conductometric titration with 0.1 N aqueous NaOH in 1:1 (vol) acetone:water mixture.[17,18] Its molecular weight was estimated from viscometric measurements in acetone at 30°C using the K and a parameters from the literature.[19] The composition of the copolymer was 1:1 (moles), in agreement with previous results.[18] The molecular weight was 110,000 g/mol.

The copolymer **II** of sodium maleate (NaM) with VA was obtained from **I** by hydrolysis with diluted aqueous NaOH solution at room temperature for 24 hours. The solution was desalted and the oligomers were removed by dialysis until the filtrate conductivity was lower than 10 μS, and the copolymer **II** was recovered by freeze-drying. It was characterized by ^1H NMR (nuclear magnetic resonance) spectra recorded in D_2O with a Bruker AM 300 MHz spectrometer and SEC. From **II,** the copolymer **III** of maleic acid (MAc) with VA was obtained by passing a dilute solution of **II** through an ion exchange column filled with Dowex 50WX 8 20–50 mesh sulfonic resins. The aqueous solution of **III** was used as such for conductometric or potentiometric titration in water with LiOH or $Ca(OH)_2$.[20] The structures of **I**, **II**, and **III** copolymers are given in Scheme 1.

The composition of the copolymer determined by conductometric titration and confirmed by ^1H NMR spectra was MAn:VA = 1:1 (mole), in agreement with the data published previously about this copolymer and other MAn copolymers.[16–18] The weight-average molecular weight (M_w) of NaM-VA, determined by SEC, was 311,000 g/mol, while that of parent MAn-VA copolymer, estimated from viscometric measurements, was 110,000 g/mol. This difference could be explained by the



Scheme 1. Chemical transformation of MAn-VA copolymer (**I**) to MAc-VA copolymer (**III**).

separation of low MW fractions during dialysis. At the same time, these values confirm that during the hydrolysis and neutralization no chain degradation occurred.

Methods

The SEC analyses were performed using a Waters 150C chromatograph equipped with a lab-made viscometer, multi-angle laser light scattering (MALLS) DSP-F from Wyatt with two Shodex columns: SB 804 HQ and SB 805 HQ.[21] The eluent was a 0.1 M $NaNO_3$ solution, the flow rate was $1.0\,cm^3\,min^{-1}$ and the feed was 0.4 mL of 1.0 g/L copolymer solution in aqueous 0.1 M $NaNO_3$. For MW calculation, the value $dn/dc = 0.151\,mL/g$ was used from refractometric measurements in $NaNO_3$ solution with a Brice Phoenix differential refractometer at $\lambda = 546\,nm$.

The conductometric titrations were carried out using a Tacussel conductometer type CD78 and a XE 130 cell. pH measurements were performed by using a Tacussel Minisis 600 apparatus with a Tacussel combined glass electrode XC 100.

The IR spectra of both copolymers after various periods of storage were recorded with a Perkin-Elmer 577 spectrometer, on KBr pellet.

To check the stability of the polymer during storage, an aqueous solution of 1.0 g/L (8.13×10^{-3} eq/L) of **II** was prepared and kept overnight; thereafter it passed through an ion exchange column to obtain a solution of copolymer **III**. From this solution, one-half was stored as such; the other was neutralized with NaOH to obtain the sodium salt **II**. We consider that this preparation can provide more stability, free of aggregate solutions. Each of these solutions was distributed into two stoppered vials, one of which was stored at 25°C (samples **IIA** and **IIIA**, respectively) and the other at 100°C (**IIB** and **IIIB**, respectively). Aliquots of 4 mL were withdrawn after 1, 2, 5, 7, 14, and 28 days from all four samples, neutralized with NaOH if necessary, and SEC chromatograms were recorded. Thus, the apparent M_w values can be compared.

RESULTS AND DISCUSSION

Generally, the polymeric C-C bond is considered to be stable in water. Polymers obtained by addition mechanism may be degraded by water only through cleavage of secondary bonds.[22,23] In solid state, the copolymer MAn-VA was found stable at 100°C, between 130 and 210°C cyclic anhydride reformation can occur, between 200 and 300°C the elimination of acetic acid takes place, and above this temperature, depolymerization and cracking reactions can be observed.[24] In aqueous solution, MAc-VA copolymer was found to be more susceptible to undergoing some chemical transformations of its reactive groups, especially deacetylation or lactonization, than the NaM-VA copolymer,[10,11] but the change in molecular weight was not reported until now.

However, we observed that SEC chromatograms recorded after various periods of time were different compared to those recorded at $t = 0$, that is, a solution prepared by gentle stirring at room temperature for 24 hours. The chromatograms of both samples stored at 25°C maintained a "clean" pattern, but the elution time increased. Some examples for both NaM-VA and MAc-VA copolymers are presented in Figure 1.

In the chromatograms of samples stored at 100°C, the volumes of elution were shifted to higher values, indicating an important decrease of M_w, as can be seen in Figures 2 and 3, representing the chromatograms of NaM-VA sample stored for 1, 2, and 5 days and of MAc-VA sample stored for 1, 5, and 28 days, respectively.

The changes in molecular weight during the storage of NaM-VA and MAc-VA copolymers at 25 and 100°C are presented comparatively in Figures 4 and 5, respectively, in which the apparent weight-average molecular weight M_w was plotted against the time of storage.

It can be seen that, generally, M_w decreases for all samples, but much more slowly at room temperature, at which the polymers still have M_w values as high as 100,000 g/mol after 28 days of storage. At high temperature, the M_w drops after 1–2 days, and a difference can be observed between two copolymers: the M_w of the Na salt decreases continuously to a very low value (3,500 g/mol), while the M_w of the acid form decreases to a minimal value of 28,600 g/mol and thereafter increases to 62,000 g/mol.

The decrease in molecular weight at 25°C could be ascribed to (i) physicochemical processes, such as the weakening of interchain interactions (hydrogen bonds or hydrophobic forces); (ii) chemical processes resulting in a chain breaking. Particularly at high temperature, a chain scission via chemical transformation can be supposed. To check the evolution during storage, IR spectra were recorded for the four samples. The spectra of samples stored at 25°C are displayed in Figures 6 and 7.

In the spectra of the NaM-VA sample recorded at $t = 0$ and after one and seven days the patterns in the characteristic region between 1000 and 2000 cm^{-1} are similar (Figure 6). Typical absorption bands appear at 1730 cm^{-1} for ester groups of acetate moieties, around 1600 and 1400 cm^{-1} for the carboxylate groups of sodium maleate moieties, at 1260 cm^{-1} corresponding to CH$-$O bond, and at 1020 cm^{-1} corresponding to O$-$C(O)(CH_3) bond from acetate moieties[11,25]. The appearance of a shoulder at 1300 cm^{-1} after seven days could be ascribed to the beginning of acetate groups hydrolysis.[11] In the spectra of the

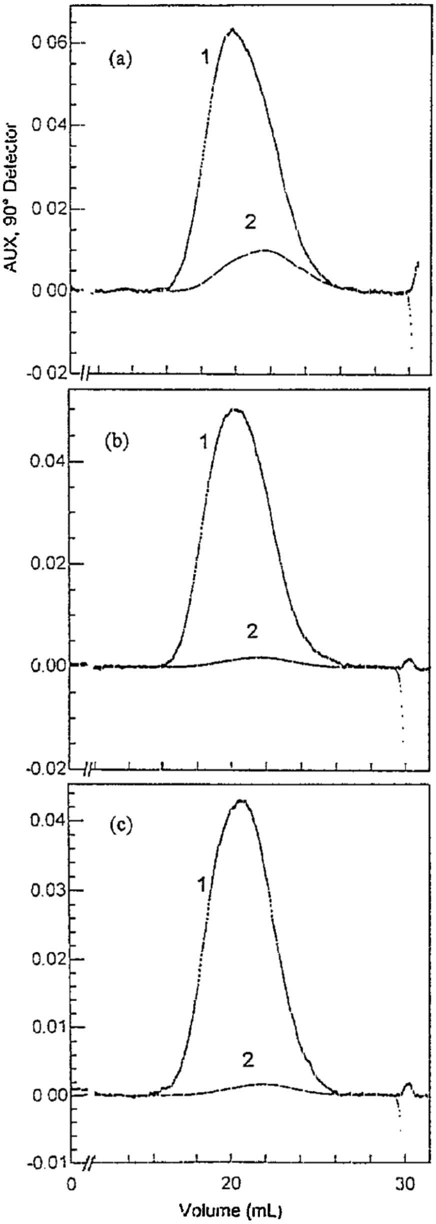


Figure 1. SEC chromatograms of NaM-VA copolymer stored at 25°C for 1 (a) and 7 (b) days and of MAc-VA copolymer stored at 25°C for 7 days (c) (measurements after neutralization). 1: light scattering detector; 2: refractometric detector.

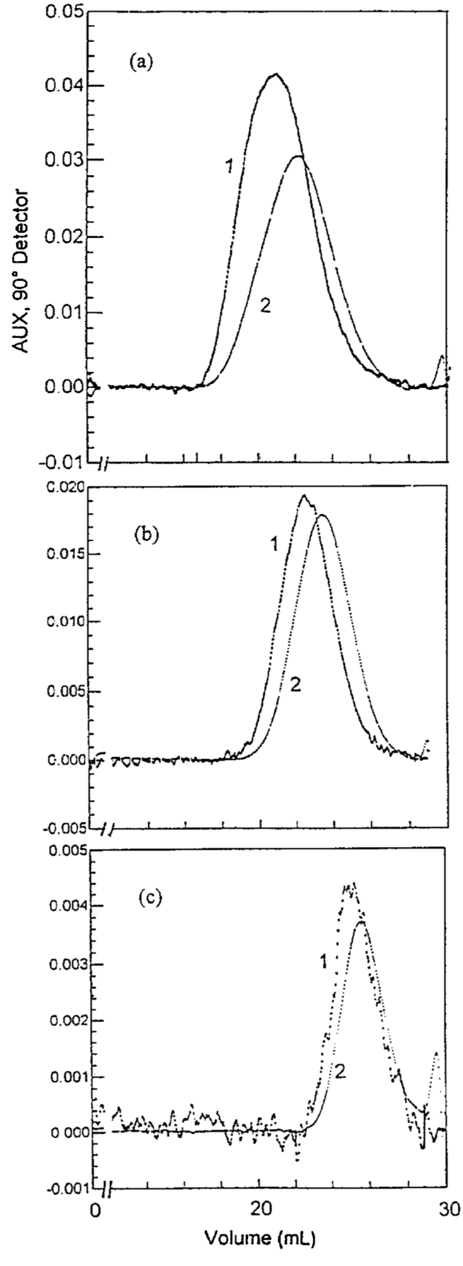


Figure 2. SEC chromatograms of NaM-VA copolymer stored at 100°C for 1 (a), 2 (b), and 5 days (c). 1: light scattering detector; 2: refractometric detector.

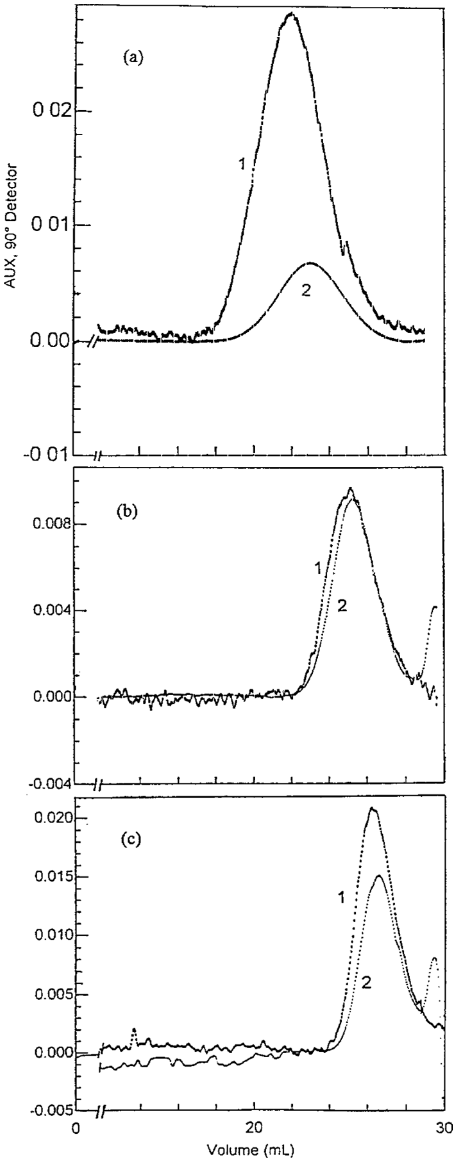


Figure 3. SEC chromatograms of MAc-VA copolymer stored at 100°C for 1 (a), 5 (b), and 28 days (c) (measurements after neutralization). 1: light scattering detector; 2: refractometric detector.

MAc-VA sample (Figure 7) the characteristic bands can be seen at 1700–1730 cm^{-1}, corresponding to the ester groups of acetate moieties and to carboxylic groups from maleic acid moieties, at 1390 and

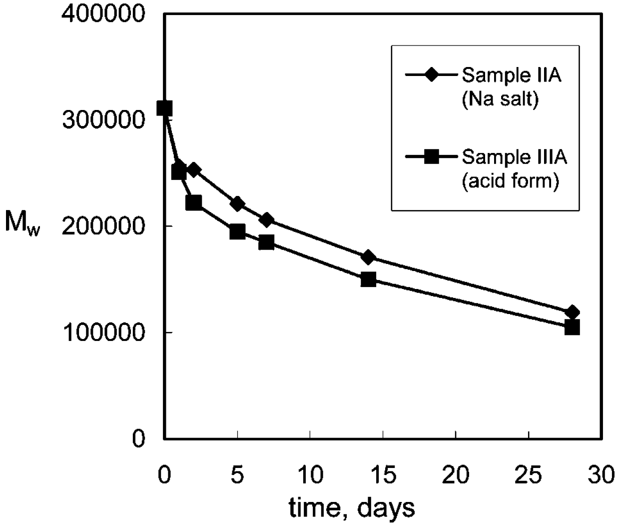


Figure 4. M_w decrease during the storage of NaM-VA and MAc-VA copolymers at 25°C.

1450 cm^{-1} due to the carboxylic groups of maleic acid moieties, at 1250–1260 cm^{-1} corresponding to CH–O bond, and at 1040 cm^{-1} corresponding to O–C(O)(CH_3) bond from acetate moieties. The spectra of stored

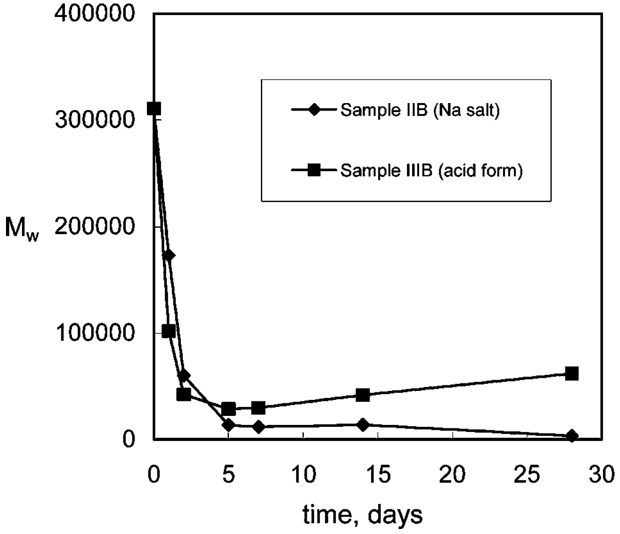


Figure 5. M_w decrease during the storage of NaM-VA and MAc-VA copolymers at 100°C.

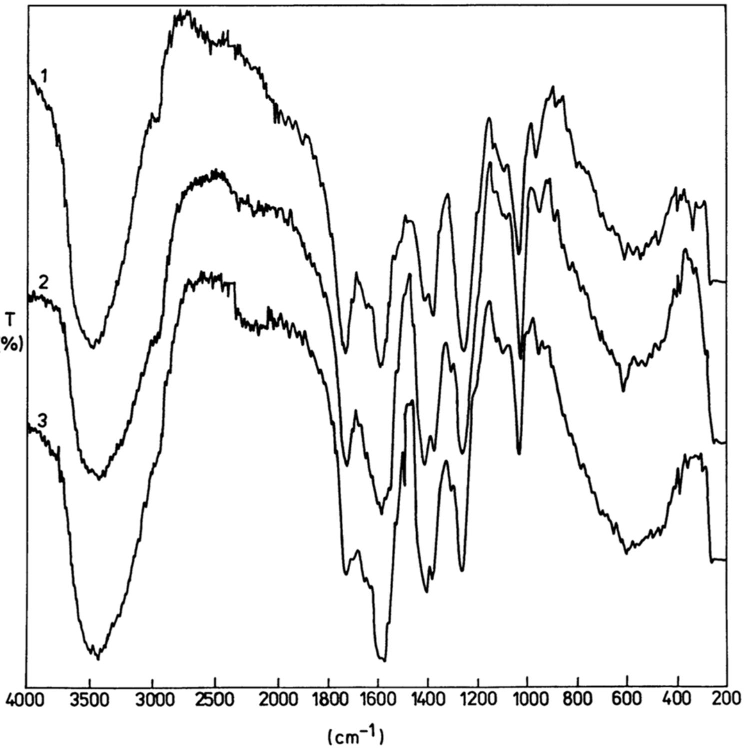


Figure 6. IR spectra of NaM-VA sample stored at 25°C. (1) at t = 0; (2) after 1 day; (3) after 7 days.

samples are essentially similar to that recorded at t = 0, excepting the shoulder at 1760 cm^{-1}, which is visible in the spectrum recorded after seven days and can be due to lactone ring formation.[11]

The decrease with time of the molecular weight of maleic acid-vinyl acetate copolymer has not been reported hitherto. For other maleic anhydride copolymers a decrease of MW was reported during chemical modification,[26,27] but not during storage. We have observed a similar behavior for other maleic acid based copolymers. In Table I are presented some data regarding the behavior of sodium salts of maleic acid-methyl vinyl ether (commercial sample), maleic acid-N-vinylpyrrolidone, maleic acid-methyl methacrylate, and maleic acid-styrene copolymers (details about their synthesis and characterization were given elsewhere.[20])

The general trend observed is a decrease in M_w, even at 25°C. This behavior could be ascribed to the diminishing of interchain interactions such as hydrogen bonding or hydrophobic forces.

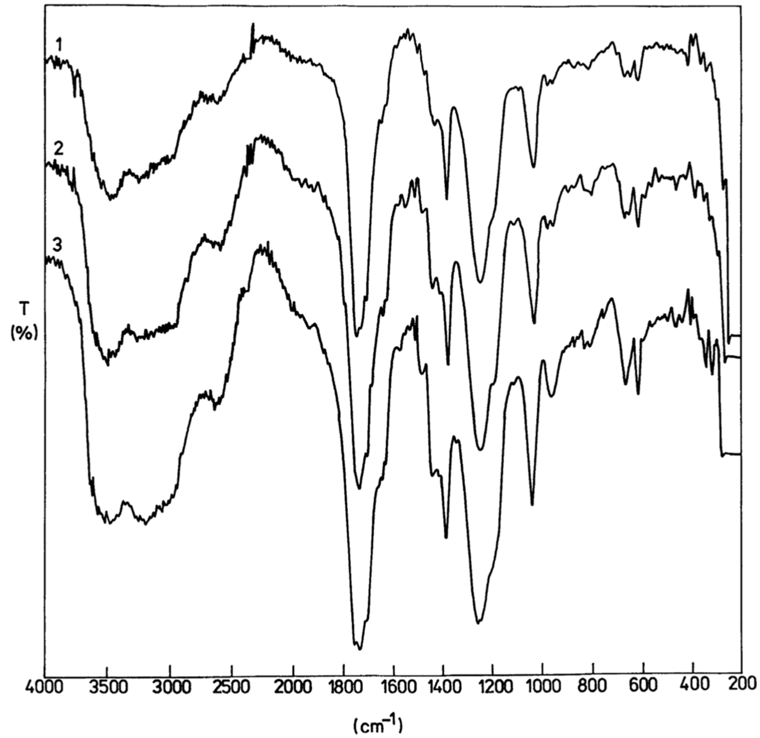


Figure 7. IR spectra of MAc-VA sample stored at 25°C. (1) at t = 0; (2) after 1 day; (3) after 7 days.

In the case of NaM-VA and MAc-VA copolymers it is less probable that hydrophobic forces will occur, the comonomer being rather hydrophilic. Concerning the hydrogen bonding, in the IR spectra of

Table I. M_w of several sodium maleate (NaM) copolymers stored in aqueous solution at 25°C

Time, days	M_w				
	NaM-MVE	NaM-VA	NaM-NVP	NaM-MMA	NaM-S
0	984,000	311,000	33,800	83,700	436,000
7	322,000	256,000	32,800	83,000	390,000
14	206,000	253,000	28,800	82,700	—

MVE = methyl vinyl ether; VA = vinyl acetate; NVP = N-vinylpyrrolidone; MMA = methyl methacrylate; S = styrene.

NaM-VA the splitting of the band at about 1600 cm^{-1} with a shoulder at 1580 cm^{-1} can be observed, which could be attributed to the appearance of free carboxylate groups, in a manner similar to that observed by Kawaguchi et al.[28] in the IR spectrum of maleic acid-isobutylene copolymer; the vibration band of free carboxylate shifts to shorter wavenumber. Also in the spectrum of MAc-VA the band at about 1700 cm^{-1} attributed to ester and carboxylic groups becomes broader as related to the appearance of free carboxylic groups.[28]

The IR spectra of samples stored at 100°C change after different periods of time, as shown in Figures 8 and 9. In Figure 8 are displayed the IR spectra of the NaM-VA sample at t = 0 and 7 days. In Figure 9 are presented the IR spectra of MAc-VA sample stored at 100°C at t = 0, 1, and 7 days.

In the spectrum of NaM-VA some important changes are observed after seven days' storage at 100°C. The band at 1730 cm^{-1} corresponding to ester groups of acetate moieties disappeared and a new band occurred

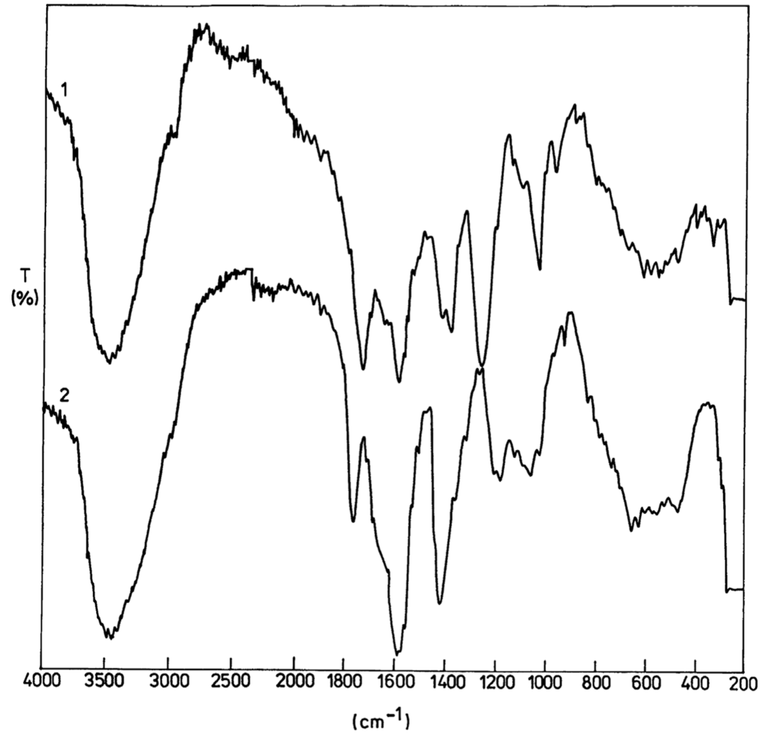


Figure 8. IR spectra of NaM-VA sample stored at 100°C. (1) at t = 0; (2) after 7 days.

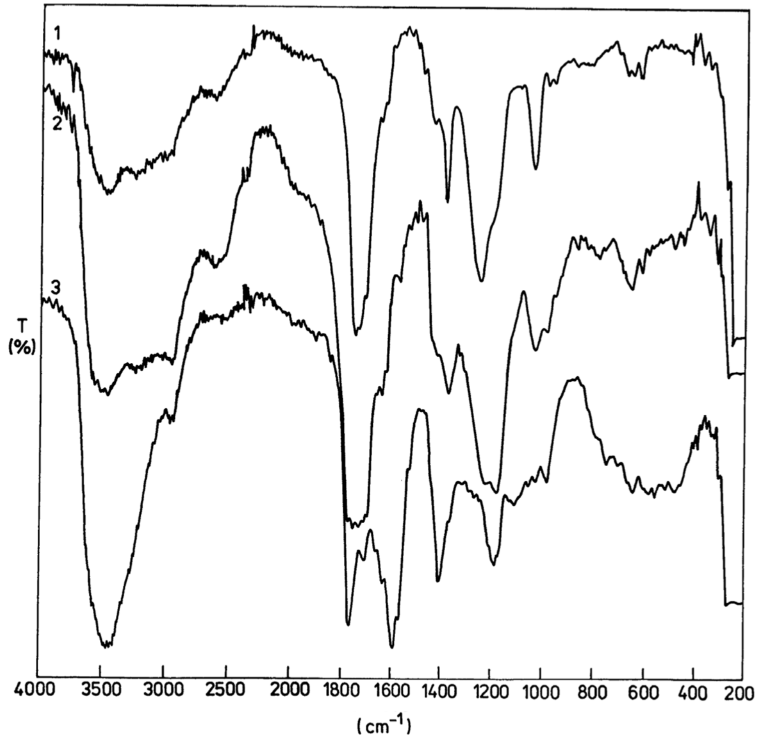
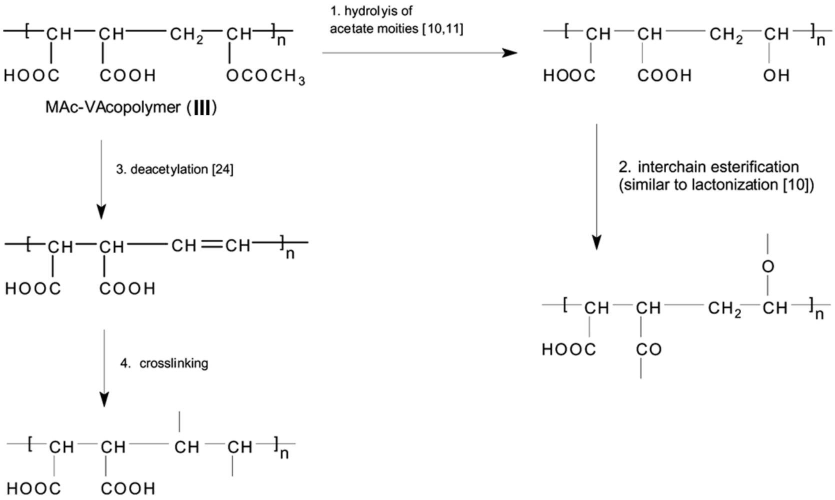


Figure 9. IR spectra of MAc-VA sample stored at 100°C. (1) at t = 0; (2) after 1 day; (3) after 7 days.

at 1760 cm^{-1}, which can be attributed to lactone rings.[11] The bands at 1600 and 1400 cm^{-1} corresponding to the carboxylate groups of sodium maleate moieties changed, but not essentially. The bands at 1260 and 1060 cm^{-1} corresponding to CH–O bond and O–C(O)(CH_3) bond from acetate disappeared or were very diminished, respectively. Some new bands occurred at 1200 and 1230 cm^{-1}, which could be attributed to primary or secondary alcohol groups, and a shoulder at 1300 cm^{-1}, which could be due to double bond formation.[25] Taking into account the changes in molecular weight correlated to IR spectra and the results already found by Dusek et al.,[11] the chemical modifications that can occur are presented in Scheme 2.

It can be seen that interchain esterification or cross-linking can increase the M_w and that these reactions were not liable to produce a gel or insoluble material. The deacetylation reaction and consequently cross-linking would be possible also for Na salt, but they are not observable by an increase of MW. A possible explanation is that the –COOH



Scheme 2. Chemical reactions occurring during the storage of maleic acid-vinyl acetate copolymer in aqueous solution.

groups allow the formation of H-bonds, which facilitate and promote the interchain reactions, while dissociated COO^- groups lead to intermolecular electrostatic repulsion.

The plot of the reciprocal of M_n versus time in the case of both samples stored at 100°C (Figure 10) gives a straight line only in the case of Na salt, corresponding to a random scission of the chain. The breaking of the chain could occur by some oxidation reaction due to the presence of VA units. Such a mechanism of degradation was proposed for methyl vinyl ether-maleic acid copolymer,[29,30] in which low molecular weight products (alcohols, aldehydes, acids) are generated and the main polymer chain is split.

It is noteworthy that some chain splitting cannot be excluded in the case of samples stored at 25°C, but it is slower so that after the longest period of time (28 days) the M_w is still as high as 100,000.

CONCLUSION

By means of size exclusion chromatography (SEC) the change of molecular weight of maleic acid-vinyl acetate and sodium maleate-vinyl acetate copolymers during storage in aqueous solution was proved. This change was a decrease or a decrease followed by some increase in M_w depending on the ionic form of the copolymer and the storage temperature. At 25°C the solutions of both copolymers are more stable, but

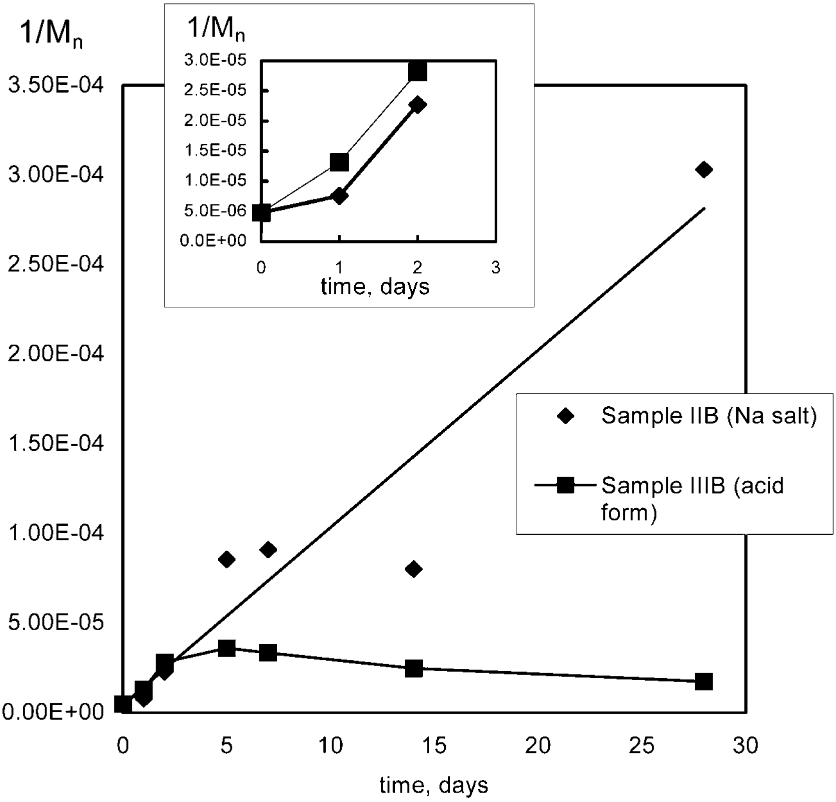


Figure 10. Plot of $1/M_n$ vs. time for NaM-VA and MAc-VA copolymers stored at 100°C.

some change was observed, attributable rather to a homogenization process. At 100°C an important, continuous decrease of MW is visible for the NaM-VA copolymer, while for the MAc-VA copolymer the SEC analysis showed a decrease followed by an increase of M_w. These differences could be related to chemical reactions, such as deacetylation, followed by lactonization, interchain esterification, or cross-linking leading to a molecular weight increase, which can occur only with the acid form. The IR spectra qualitatively confirmed the SEC results. It is concluded that SEC analysis is a rapid and convenient method that allows assessing not only the decrease, but also the increase of molecular weight. These data can be useful in the application of these copolymers especially in the biomedical area, where aggregation or degradation phenomena can influence the activity of the polymer and give secondary effects.

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