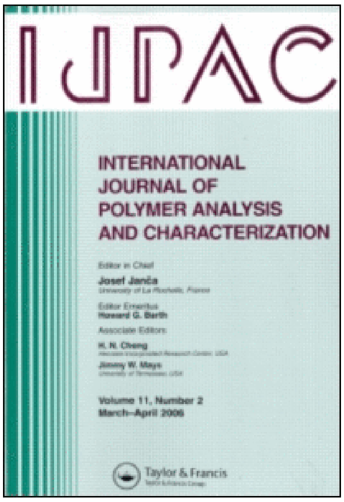

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Review: Analysis and Characterization of Maleic Copolymers

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We review the methods and techniques used for the analysis and characterization of copolymers of maleic anhydride with different vinylic or acrylic monomers. The data are arranged according to four topics, namely: determination of the composition and the distribution of the monomer sequences; determination of molecular weight and molecular weight distribution; thermal properties; physicochemical behavior of maleic acid copolymer aqueous solutions.

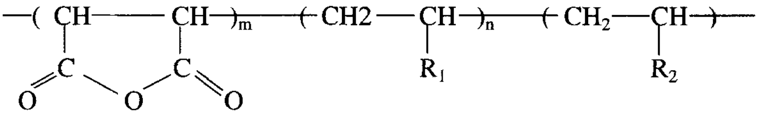
Keywords: Maleic anhydride copolymers, copolymer composition analysis, copolymer sequence distribution, Mark-Houwink-Sakurada parameters, thermal analysis, maleic acid polyelectrolytes

INTRODUCTION

Maleic anhydride copolymers with different vinylic or acrylic monomers are interesting from both the theoretical and practical points of view. After a period of growth during the 1960s and 1970s and then a relative stagnation, in recent years an increased interest in this class of compounds has been observed.[1–3]

Maleic anhydride (MA) homopolymerizes only under energetic conditions, but copolymerizes quite easily, and binary, as well as ternary copolymers or multipolymers with the following general formula are obtained:

*Corresponding author.

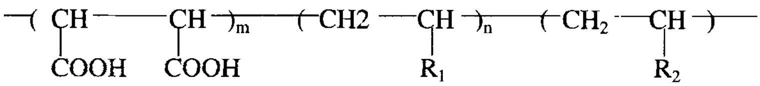


(1)

with m,n $\neq$ 0, m = n or m $\neq$ n and p = 0 or p $\neq$ 0; R_1 and R_2 are different substituents

The copolymerization mechanism of MA is different from the classical one because MA, which is an electron acceptor, can form, with donor monomers, charge-transfer complexes (CTC). Depending on the comonomer, the CTC participates, more or less, in chain propagation reactions, so that MA copolymers generally have a predominantly alternating structure.

By hydrolysis of the anhydride ring, maleic acid copolymers are obtained, with general formula:



(2)

with m,n $\neq$ 0, m = n or m $\neq$ n and p = 0 or p $\neq$ 0. Due to the presence of carboxylic acid groups they behave as anionic polyelectrolytes.

Chemical reactions on MA copolymers are an alternative to the copolymerization reactions, by which new classes of maleic copolymers with functional groups can be obtained. MA, which has a carbon-carbon double bond and an anhydride group, is a versatile compound from which can be produced a large number of low molecular or macromolecular products. Besides the above mentioned hydrolysis reaction, many other chemical reactions can be performed on MA copolymers. Reactions with alcohols or amines, including ones with biological activity (drugs) were studied.[4,5]

The synthesis of the described maleic copolymers and their derivatives has benefited from data generated in some analysis and characterization studies.[3] The studies concerning the copolymerization mechanism of MA have emphasized the composition, sequence distribution, and stereostructure. The determination of the molecular weight and molecular weight distribution, and the investigation of the thermal properties, are also important both for theoretical studies and for practical uses of the copolymers.

In this paper, results concerning the analysis and characterization of the MA copolymers obtained by radical polymerization, and their derivatives, grouped according to the method used will be presented and discussed. The analysis and characterization of unsaturated MA polyesters and MA grafted polymers was not reviewed.

Determination of the Composition and Distribution of the Monomer Sequences

Chemical Methods

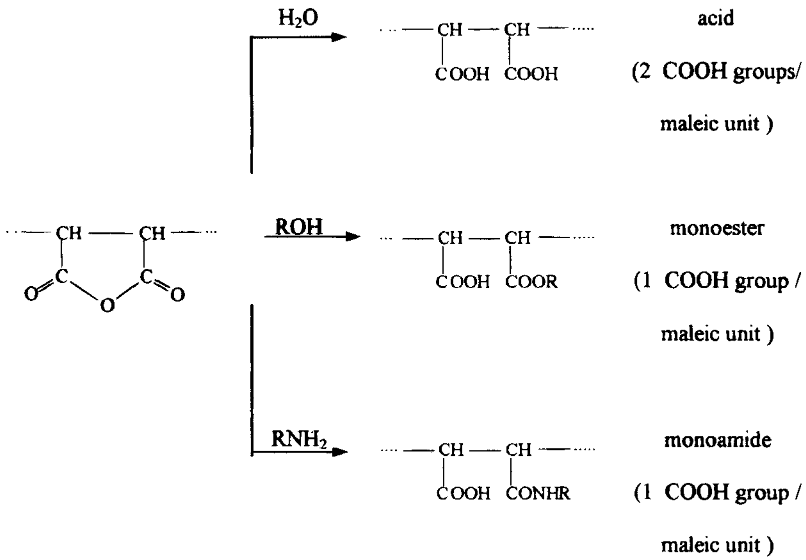
Determination of the chemical composition of MA copolymers by elemental analysis is common.[6-17] Generally, the results obtained are confirmed by other electrochemical or spectroscopic methods. Some authors compared the results of the C, H, O content (N and S content, if needed) with the calculated data corresponding to a copolymer composition of 1 : 1 moles. This approach is approximate because there are some MA copolymers with a ratio between the comonomers different from 1 : 1. When the polymer retains water, the theoretical composition was calculated on the basis of the formula: $[MA]_x[comonomer]_y[H_2O]_z$.

The analysis of the functional groups by titration was also used to determine the composition of MA copolymers. Thus, for a MA-vinyl acetate copolymer, the determination of the composition includes: determination of the anhydride groups by acid-base titration of the carboxylic acid groups formed after the reaction with aniline; determination of the total amount of carboxylic acid groups by acid-base titration adding pyridine; determination of the acetyl groups by deacetylation and titration with aqueous NaOH of the resulting acetic acid.[19]

Electrochemical Methods

After hydrolysis, monoesterification or monoamidation, the anhydride units of MA copolymers give rise to carboxylic acid groups:

The acid-base titration of the carboxylic acid groups in the presence of an indicator, *e.g.*, phenolphthaleine, gives an inconclusive endpoint. The use of instrumental methods based on electrochemical properties, such as conductometry or potentiometry, proved to be more suitable with regard to the sensitivity and reproducibility of the results. The titration is performed in organic solvents, organic solvent mixtures or organic solvent-water mixtures. The acid-base titration must be carried out in a homogeneous medium. A proper solvent should be chosen to insure solubility for both the analysed copolymer and the salt produced during the titration. In some cases an excess of reagent is added, which is back titrated, but this alternative was shown by Brown *et al.* [30] to be less accurate than a direct titration.



SCHEME 1 Hydrolysis, monoesterification and monoamidation of a maleic anhydride copolymer.

Table I summarizes results on the determination of the composition of MA copolymers via electrochemical methods.

To determine the composition of MA copolymers radioactivity measurements were also used.[13,34]

Optical and Magnetic Spectroscopic Methods

Spectroscopic methods used to characterise MA copolymers include: ^{1}H and ^{13}C nuclear magnetic resonance (NMR), infrared (IR), ultraviolet-visible (UV) and fluorescence spectroscopies. By these methods, the composition of binary and ternary MA copolymers, and, under certain conditions, the distribution of monomer sequences and the configuration of the polymer chain can be determined.

^{1}H NMR Spectroscopy permitted the confirmation of the chemical structure of MA copolymers,[22,35,36] the determination of composition for some MA copolymers with 2-vinylnaphthalene,[9] 2-cyclohexyl-1,3-dioxepin-5-ene and its derivatives[37] or tri-O-acetyl-D-glucal[17] and the investigation

TABLE I Electrochemical Methods Used to Determine the Composition of MA Copolymers

Method of analysis	*Solvent / reagent*	*Titrant*	*Copolymers*	*Ref.*
Conductometry	acetone-water	aq. NaOH	MA-E, MA-VA, MA-IBVE	[11,20–23]
		$(C_2H_5)_4NOH$ in pyridine	MA-MMA	[24]
	methanol-DMF / n-butylamine	$NaOCH_3$ in methanol	MA-alkylvinyl ethers	[25]
Potentiometry	acetone-water	aq. NaOH	MA-VA, MA-VC MA-MMA, MA-MeA	[18, 26]
	DMF	$NaOCH_3$ in DMF-methanol	MA-MMA, MA-TAG	[17,18,27]
	DMF-DO / excess of n-butylamine	$HClO_4$ in anhydrous acetic acid	MA-S, MA-P, MA-VA	[28,29]
	acetone-ethanol/ aniline	NaOH in ethanol	MA-S, MA-VA, MA-MMA, MA-A, MA-EC	[30–33]

E = ethylene; VA = vinyl acetate; IBVE = isobutylvinyl ether; MMA = methyl methacrylate; S = styrene; P = propylene; A = anethol; EC = ethyl cinnamate; TAG = tri-O-acetyl-D-glucal; MeA = methyl acrylate; VC = vinyl chloride; DMF = dimethyl formamide; DO = dioxane.

of the microstructure of MA copolymers with vinyl acetate,[36] methyl methacrylate,[24] and isobutylene.[38,39] The characteristic chemical shift for the MA protons appears between 3 and 4 ppm.

^{13}C NMR Spectroscopy proved to be a very useful technique for the structural analysis of polymers because of the simplicity of spectra and the wide range of chemical shifts. For MA copolymers ^{13}C NMR spectroscopy makes it possible for the determination of composition[40,41] from the ratio of the integrals of some well resolved and correctly assigned shifts. The monomer sequences and information about the microstructure of some MA copolymers can also be obtained by ^{13}C NMR spectra. In this case special techniques are used to accurately generate some more simple subspectra, *e.g.*, the DEPT technique (distorsionless enhancement by polarization transfer).[40] The results concerning the evaluation of sequence distribution and that of microstructure of MA copolymers by means of ^{13}C NMR spectroscopy are summarized in Table II.

This method has identified a non-alternating distribution of monomers in copolymers previously considered as alternating. This must be

TABLE II The Estimation of Sequence Distribution and Microstructure of MA Copolymers by ^{13}C NMR Spectra

Copolymer (composition, moles)	*Chem. shift (ppm)*	*Assignment*	*Results*	*Ref.*
MA-styrene (1:1; 1:2; 1:3)	144 142 138 137	SSS triads SSM triads MSS triads SMS triads	39% alternating triads and 58% semi-alternating triads in a copolymer with MA:S = 1:1	[42]
MA-styrene (1:1.03)	144 142 138 137	SSS triads SSM triads MSS triads SMS triads	89% alternating triads 8% semi-alternating triads	[43]
MA-styrene (between 1:1 and 1: 1.89)	33–37 37–42 42–47	SMS triads SSM + MSS triads SSS triads	*e.g.* 88% alternating triads 12% semi-alternating triads in a copolymer with MA:S = 1:1.07	[40]
MA-styrene (between 1:1 and 1:1.89)	33–37 37–42 42–47	SMS triads SSM + MSS triads SSS triads	analysis of mechanism of copolymerization	[44–46]
MA-p-methoxy-styrene (not specified)	33–37 37–42 42–47 52 52.8	SMS triads SSM + MS S triads SSS triads cis configuration trans configuration	almost entirely alternating cis : trans = 1.33 : 1	[47]
MA-p-chloro-methylstyrene (not specified)	33–37 38–42 42–45 51.5 53	SMS triads S SM+MSS triads SSS triads cis configuration trans configuration	almost entirely alternating cis : trans = 0.73 : 1	[48]

In triads, M = maleic anhydride; S = styrene

expected for MA-S copolymers synthesized from non-equimolar monomer feeds and/or at higher reaction temperatures, which possess a far from 1:1 molar composition.[42] For other MA-S samples with mole fractions of styrene between 0.51 and 0.65, it can be observed that alternating triad fractions are between 88 and 14%. In this case the copolymerization conditions are incompletely specified by the authors. It would be desirable to analyze by the ^{13}C NMR DEPT method some copolymers with 1:1 molar ratios but different monomer distributions. At the same time, lower contents of alternating triads can indicate a mechanism of copolymerization involving participation of both CTC and free monomers in the propagation process.[43-46] The signal for C atoms from C=O groups of MA units appears, for different copolymers, at 171–173; 172–174; 173; 171.5–171.8; 173–178 ppm, depending on the anhydride ring environment.[22,27,42,48,49] The peak for methine carbons from MA units appears at 42–52 ppm. ^{13}C NMR DEPT method was also used for the characterization of citraconic anhydride copolymers.

IR spectroscopy was used to identify or to confirm the structure, to determine the composition and to investigate the microstructure of MA copolymers[14,15,25,50–56]. The characteristic bands for the maleic anhydride ring in copolymers and for the derivatized groups–carboxyl or carboxylate, ester, amide group–are presented in Table III.

The most significant for the maleic rings are the peaks at about 1850 and 1780 cm^{-1}. The exact position of these peaks depends on the comonomer:vinyl acetate, methyl methacrylate, methyl acrylate, styrene, ethylene, N-vinylpyrrolidone, ethyl vinyl ether.[15,22-24,52, 53,69]

IR spectroscopy is also used for the quantitative analysis of some binary or ternary MA copolymers, using the integrated absorbtivities of some characteristic bands.[51,55,61] For the MA units the integral was extended from 1760 to 1920 cm^{-1},[51,55,61] and for the maleic acid or ester units the integral ranged between 1667 and 1770 cm^{-1}.[51] The comonomers in the investigated copolymers were styrene, with the characteristic bands for the

TABLE III Characteristic Bands of IR Spectra for the Anhydride Ring and for the Derivatized Groups in Maleic Copolymers

Characteristic band (cm^{-1})	*Assignment*	*Ref.*
920, 935	chain vibration (CH_2, CH)	[27,46,52]
1020, 1080	stretching vibration of C–O–C in anhydride	[52]
1220	idem	[15,27,52,53]
1760, 1780	stretching vibration of C=O in anhydride	[15,22,24,25,39, 41,52,53,57,58,69]
1825, 1850	idem	[15,22,24,25,27, 52,53,58,69]
1165, 1200	characteristic bands for ester	[9,58]
1725, 1730	stretching vibration C=O of ester	[41,51,57,59]
1556, 1654	characteristic bands for amide	[60]
1700 –1730	stretching vibration C=O of acid	[54]
1571	characteristic band for amide	[54]
1590	characteristic band for COO^- involved in a hydrogen bond	[54]

phenyl ring between 660 and 720 cm^{-1},[55,61] and 2-ethylhexyl acrylate or methyl methacrylate with characteristic bands for the esters at 1660–1760 cm^{-1}.[55,61]

Information about the copolymer microstructure can be obtained from certain characteristic bands. Thus, a peak at 725 cm^{-1} in the MA-ethylene copolymer spectrum arises from a tetramethylene sequence.[15] The signals at 1060, 1140 and 1190 cm^{-1} in the MA-methyl methacrylate copolymer spectrum correspond to sequences of at least three methyl methacrylate units.[24,52]

UV spectroscopy allowed the characterization of the charge transfer complex formed between MA and the comonomer.[12,21,31,33,45,59] Also, from UV spectra the composition of some MA copolymers with comonomers which absorb in UV range, such as vinylnaphthalene[10] or N-vinylcarbazole[61,62] can be determined, using 2-ethylnaphthalene or poly(N-vinylcarbazole) as standard. For chemical reactions on some MA copolymers, the conversion can be followed by UV spectroscopy, using the extinction coefficients determined from model compounds.[58] Together with other methods, UV spectroscopy offers information on the dissociation and hydrogen bond formation in maleic or citraconic acid copolymers.[25,54]

Fluorescence spectroscopy gives information on the sequence distribution in MA copolymers with comonomers which show fluorescence, like 2-vinylnaphthalene,[7-9] 2-isopropenylnaphthalene[10] or N-vinylcarbazole.[62] It was found that, although these copolymers have equimolar composition and are considered alternating, they contain diad fractions of 2-vinylnaphthalene or N-vinylcarbazole.

Determination of the Molecular Weight and Molecular Weight Distribution

Classical methods for the determination of molecular weight of the polymers are based on osmometric, light scattering or viscometric measurements. In addition, size exclusion chromatography (SEC) has become a useful technique for the rapid determination of the molecular weight (MW) and molecular weight distribution (MWD) of polymers. Without presenting the theoretical basis for these methods, which are already well-known and widely applied, we will describe their use to determine MW and MWD of MA copolymers or their derivatives.

Osmometry

Membrane osmometry (MO) or ebulioscopy was used to determine MW of some MA copolymers with styrene,[64,65] ethylvinyl ether,[66,67] β-methylstyrene,[6] octyl monoitaconate,[68] and tri-O-acetyl-D-glucal.[17] In most of these cases, this method was used as an absolute method to establish some Mark-Houwink-Sakurada equations, from which the MW of "unknowns" can be determined by viscometric measurements. It is known that by osmometric measurements the number average MW (M_n) is obtained, while from light scattering the result is the weight average MW (M_w). M_w is closer to the viscometric MW, compared with M_n. Only in the cases of narrow MWD of samples or when M_w is difficult to obtain (such as MW is too low), can M_n be used reasonably to establish the MHS equation. At the same time, osmometry and other methods like light scattering permit the study of copolymer solution properties (the dimension and shape of macromolecules and their interactions in solution). A relationship between the second virial coefficient A_2 and M_n was found for the MA-vinyl acetate copolymer in THF as follows: $A_2 = 9.11 \times 10^{-3} M_n^{-0.27}$ (A_2 in units of $mL \cdot mol \cdot g^{-2}$).[72] The value of the exponent is comparable to those obtained for flexible polymers in good solvents (–0.1 ~ –0.3).[66]

Light scattering

Static light scattering (LS) was also used to determine the MW and to establish some Mark-Houwink-Sakurada equations for maleic copolymers.[66,67,69,70] Unperturbed dimensions, persistence lengths, and interactions in solution were studied with this method[65,67,72-74] in different organic solvents. In Table IV b the unperturbed dimensions and the steric parameters of some MA copolymers with styrene, isobutyl vinyl ether, methyl methacrylate, ethyl vinyl ether and monoethyl itaconate are presented. The rather small values of these parameters could be explained in terms of a separation of the side chains by the MA units, giving a greater flexibility of the copolymer chain because of weakening of the interaction between the side chains.[65,66,68] Another conformational parameter is the characteristic ratio defined as $C_\infty = lim_{\to\infty} (\langle r^2 \rangle_0 / n\, l^2)$, where n is the number of main chain bonds of length 1. This value was obtained to be 6.5 for a copolymer MA-ethyl vinyl ether in THF at 25°C.[67] The relationship between A_2 and M_w for this copolymer corresponded to that expected for flexible polymers in good solvents.[66]

TABLE IVa K and a for MA Copolymers

Copolymer	Solvent	Temp. °C	K,mL/g	a	MW range	Ref.
MA-S†	THF	30	5.07×10^{-3}	0.81	1.32×10^5	[65]*
	acetone	30	8.69×10^{-3}	0.74	—	
					7.5×105	
MA-VA‡	THF	30	7.17×10^{-3}	0.76	—	[72]**
	acetone	30	9.32×10^{-3}	0.94		
MA-IBVE§	THF	30	7.56×10^{-2}	0.55	21×10^4–	[73]*
	acetone	30	12.47×10^{-2}	0.506	111×10^4	
	butanone	30	11.94×10^{-2}	0.512		
MA-EVE†	acetone	30	2.22×10^{-3}	0.582	3×10^4– 5×10^5	[66]*
MA-MMA§	THF	30	13.4×10^{-3}	0.69	20×10^4–	[74]*
	acetone	30	12.4×10^{-3}	0.69	71×10^4	
	dioxane	30	26.1×10^{-3}	0.64		
	DMSO	30	7.5×10^{-5}	0.77		
MA-OMI‡	THF	25	7.4×10^{-3}	0.71	4×10^4	[68]***
	ethanol	25	2.2×10^{-2}	0.60	5×10^5	
	1-propanol	25	3.28×10^{-2}	0.55		
	methanol	25	3.50×10^{-2}	0.54		
	1-butanol	25	3.60×10^{-2}	0.52		
	2-propanol	25	3.80×10^{-2}	~0.50		

S = styrene; VA = vinylacetate; IBVE = isobuthyl vinyl ether; MMA = methyl methacrylate; EVE = ethyl vinyl ether; OMI = octyl monoitaconate; THF= tetrahydrofuran; DMSO = dimethylsulfoxide; copolymer composition: † very close to 1:1 (moles); ‡ not specified; § copolymers claimed as "alternating copolymer"; absolute method used to determine MW of MA copolymers: *LS; ** MO; *** EC

TABLE IVb Unperturbed Dimensions and Steric Parameters for MA Copolymers

Copolymer	Solvent	Temp. °C	$K_o \times 10^4$ mL/g	$(<r_o^2>/M)^{1/2} \times 10^4$, nm	σ	Ref.
MA-S	THF				1.91	[65]
	acetone				1.91	
MA-IBVE	THF	30	12.9	850	2.21	[73]
	acetone	30	12.9	850	2.21	
MA-MMA	THF	30	9.03	755	1.96	[74]
	acetone	30	7.94	723	1.88	
	dioxane	30	11.09	808	2.10	
	DMSO	30	12.23	835	2.17	
MA-EVE	THF	30	5.7	—	—	[67]
MA-MOI	THF	25	4.9	581	2.47	[68]
	ethanol	25	4.9	581	2.47	
	1-propanol	25	4.9	581	2.47	
	methanol	25	4.9	581	2.47	
	1-butanol	25	4.0	542	2.30	
	2-propanol	25	4.0	542	2.30	

K_o=conformational parameter from Stockmayer-Fixman eq.; σ = steric parameter; THF=tetrahydrofuran; DMSO=dimethylsulfoxide; S=styrene; IBVE=isobutyl vinyl ether; MMA=methyl methacrylate; EVE=ethyl vinyl ether; MOI=monooctyl itaconate.

Dynamic light scattering gives information on conformational transitions, intermolecular interactions, and aggregation phenomena.[10,58,71,124] Due to the various important information about copolymer characterization obtained by this method, it can be inferred that it has not been sufficiently exploited until now to study MA copolymers.

Viscometry

This method is very useful to estimate MW of polymers, due to its accessibility, simplicity and rapidity. The practice of this method usually consists of measuring the flow times for the solvent and dilute polymer solutions in a capillary viscometer. Using a simple mathematical and graphical treatment, the intrinsic viscosity or Staudinger index [η] is determined, which is connected to the MW (M_v is viscosity average MW) by Mark-Houwink-Sakurada equation:

$$[\,\eta\,] = K \cdot M^a \text{ or } K \cdot M_v^a \tag{1}$$

where K and a are constants related to macromolecule conformation in solution and depend, for a specific polymer, on solvent and temperature. To determine K and a, MWs of a series of different MW polymer fractions with narrow MWD are measured using an absolute method such as osmometry or light scattering. K and a are graphically obtained. In Table IVa K and a values for different MA copolymers are presented.

Unperturbed molecular dimensions $(\langle r_o^2 \rangle / M)^{1/2}$ and the steric parameter σ can be estimated from the intrinsic viscosities using the Stockmayer-Fixman equation[125] In Table IVb such results are presented for MA copolymers.

In Table V K and a values for maleic acid (MAc) copolymers are presented.

Size Exclusion Chromatography (SEC) In 1976 a SEC technique was first developed to determine MW and MWD of MA-styrene copolymers[77]. In recent years this method has been almost exclusively used for determining MW and MWD for different MA copolymers.[7-10,59,62,63,68,78-83] In most cases tetrahydrofuran was used as solvent. It is know that SEC is a relative method, the results usually being evaluated based upon calibration with linear polystyrene standards with narrow MWD, or sometimes with poly(methyl methacrylate)[58]. When MA-styrene copolymers are used as standards[77,80] or when SEC is coupled with LALLS (low-angle laser light scattering),[81,82] absolute values of MW are obtained. In some cases, these values fall on an universal calibration curve,[77,82,83] supporting the hypothesis that viscometric

TABLE V K and a Constants for Maleic Acid Copolymers

Copolymer	*Solvent*	*Temp. °C*	*K,mL/g*	*a*	*Ref.*
MAc-EVE*	DO + water	30	4.148×10^{-3}	0.565	[66]
	THF	30	1.838×10^{-3}	0.661	
MAc-EVE*	water + NaCl 0.01M	30	0.59×10^{-3}	0.919	[66]
Na salt	0.18M	30	0.68×10^{-3}	0.805	
	0.50M	30	1.00×10^{-3}	0.732	
	1.00M	30	4.24×10^{-3}	0.608	
	2.00M	30	4.68×10^{-3}	0.599	
	4.00M	30	4.49×10^{-3}	0.593	
MAc-NVP†	water + HCl pH = 2.07	25	3.25×10^{-2}	0.62	[75]
MAc-S*	water $\alpha = 0.1$	25	1×10^{-5}	0.98	[76]
	0.2	25	5.1×10^{-4}	0.87	
	0.4	25	1.63×10^{-2}	0.70	
	0.5	25	3.73×10^{-2}	0.67	
	0.65	25	1.47×10^{-1}	0.61	
	0.80	25		0.60	
	0.95	25	2.79×10^{-1}	0.59	
			3.95×10^{-1}		
MAc-NaSS*	water + NaCl 0.1M,	25	7.65×10^{-4}	0.924	[56]

EVE = ethylvinyl ether; NVP = N-vinylpyrrolidone; S = styrene; NaSS = sodium styrene-sulphonate; DO = dioxane; α = neutralization degree; copolymer composition: * very close to 1 : 1 (moles); † not specified.

hydrodynamic volume, characterized by $[\eta]$ M_w, is the controlling factor in determining separation in SEC. In the case of maleic acid copolymers that behave as polyelectrolytes, it is necessary to use a pH 9 buffer system modified with 0.2 M $LiNO_3$ as mobile phase, to avoid adsorptive and electrostatic effects.[81] Also to prevent specific adsorption and/or repulsion of the MA-styrene copolymer to the column material, tetrahydrofuran with 5% anhydrous acetic acid is used as mobile phase.

Thermal Analysis

The thermal behavior of MA copolymers was studied using pyrolysis-gas chromatography (PGC), thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). PGC allowed the evaluation of composition for MA-styrene copolymers with 50,67 and 75% moles styrene using a linear relationship between the styrene content in copolymer and in pyrolytic products respectively.[117] The low styrene content in pyrolysis products for MA-styrene 1 : 1 copolymer was assigned to a predominantly alternating distribution of the comonomers.[118]

DSC is used to determine the glass transition temperature T_g, which is a characteristic parameter for an amorphous polymer. The T_g of a copolymer is sensitive to the mode of arrangement of the comonomers as well as their stereochemistry. The results obtained by DSC for different MA copolymers, containing equimolar amounts of MA and the comonomer, showed that T_g depends on comonomer nature, for example.[119]

Copolymer	**TRg, C**
MA-styrene	124-127
MA-vinyl acetate	75-76
MA-ethyl vinyl ether	68-69
MA-butyl vinyl ether	56-57

For each copolymer, T_g values observed for a set of samples obtained from different ratios of comonomers are constant. Thus, the authors suggest the formation of alternating arrangements of comonomers.

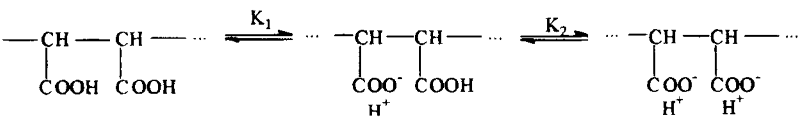
The incorporation of MA increases the thermal stability of a MA-methyl methacrylate copolymer compared to methyl methacrylate homopolymer.[27] The TG analysis of some MA copolymers has generated data on the thermal stability, mechanism of decomposition and microstructure of copolymers.[27,36,121] Recent data on the TG, derivative thermogravimetry (DTG) and PGC analysis of some MA-styrene copolymers indicated a clearly different behavior for statistical, alternating and block copolymers.[122] The main decomposition products identified by PGC are styrene, benzene, toluene and ethyl benzene. The yield of these products varies greatly with the type of copolymer and the temperature. The apparent thermal stability of MA-styrene copolymers decreases in the order: alternating, random and block.[122a] Also, the pyrogram of a random MA-vinyl acetate copolymer is very much different from that of an alternating copolymer of the same composition.[122b]

Physicochemical Behavior of Maleic Acid Copolymer Aqueous Solutions

As mentioned previously, in water the anhydride ring hydrolyses, so that maleic acid copolymers are obtained. The carboxyl groups can dissociate, giving rise to charges on the macromolecular chain, so that the copolymers behave in aqueous solution as polyelectrolytes (PEL). PELs are water soluble polymers that carry ionized or ionizable groups. In aqueous solution they are dissociated into macroions (polyions) and ions of opposite charge–counterions. To depict the PEL behavior in solution, several models were proposed, which describe the counterion distribution around the polyions and their properties in solution.[84-87]

The polyelectrolyte solution behavior of maleic acid copolymers (maleic polyelectrolytes) was studied using several techniques: potentiometric titration,[76,88-91,97,98,100-108,110] viscometry,[76,89,98,103-104,107] calorimetric studies,[101-103] dilatometry,[76,102,105] UV spectroscopic studies,[99,103,109] and electrical conductivity measurements.[108] Some characteristic features were discerned: the two-step dissociation and binding of counterions, conformational transitions induced by pH variation, a specific behavior of the viscosity exhibiting a maximum at the half-neutralization point, and characteristic phase separation.[111-114] These properties are related, on one hand, to electrostatic interaction between adjacent carboxyl groups of maleic acid units, and on the other hand, to hydrophobic interactions between non-polar segments. The dissociation of maleic acid copolymers is the main factor responsible for the polyelectrolyte behavior in aqueous solution.

MAc copolymers exhibit characteristic potentiometric titration curves[88-90,97-105] corresponding to two-step dissociation of carboxylic acid groups:



SCHEME 2 Two-step dissociation of carboxylic acid groups in a maleic acid copolymer

The difference between pK_1 and pK_2 is about 3 to 5 units. This important difference can also distinguish between MAc and fumaric acid.[115]

	pK1	**pK2**
maleic acid	1.83	6.02
fumaric acid	3.03	4.44

The acidity of first carboxylic acid group is stronger due to the inductive effect of adjacent carboxylic acid group. The presence of neighboring dipoles promotes the ionization of carboxylic acid groups. For example, in a compound like $R\text{-}CH_2\text{-}COOH$, $pK_a = 4.87$ when $R = CH_3$ and $pK_a = 1.7$

when R = COOH.[88] The second carboxylic acid group is much less acidic, due to the repulsive effect of the ionized adjacent group and to the stabilization of the monoanion by an intramolecular hydrogen bond.

Dissociation constants $pK_{a,1}$ and $pK_{a,2}$ were determined for different MAc copolymers[89,90,116] by potentiometric titration. It was observed that the addition of an electrolyte with low molecular weight induces an increase in dissociation, as a result of screening of repulsive electrostatic interactions. The apparent dissociation constant can be expressed depending on intrinsic dissociation constant pK_a^0 (pK_0) by the equation.[92]

$$pK_a = pK_a^0 + (0.434/RT)(\partial G/\partial \alpha) \tag{II}$$

where G is the free electrostatic energy and α is the degree of neutralization. For MAc copolymers a titration equation was developed that takes into account the two-step dissociation.[97,98,104,105] The titration curves can be analysed using a greater number of successive ionization constants[93,95] and the conformation of dissociated maleic polyelectrolytes can be investigated using a Monte Carlo simulation method.[96] Table VI presents the pK_1^0 and pK_2^0 constants determined for different MAc copolymers.

It is noticeable that the first dissociation step is characterized by pK_1^0 values in the acid range, while for the second dissociation step pK_2^0 values are situated in the basic range. The dissociation constants are influenced by the nature of the comonomer and by side chain size. The first carboxylic acid

TABLE VI pK_1^0 and pK_2^0 Constants for Maleic Acid Polyelectrolytes Determined by Potentiometric Titration

*Copolymer**	pK_1^0	pK_2^0	*Ref.*
MAc-ethylene	3.65	6.40	[88]
	3.80	—	[101]
MAc-propylene	3.40	7.40	[88]
	3.50	—	[101]
MAc-isobutylene	2.72	8.83	[88]
	3.00	9.20	[107]
MAc-2-methylpentene	—	9.35	[88]
MAc-styrene	—	7.75	[88]
	3.30**	—	[76]
MAc-ethylvinyl ether	3.5	6.6	[98,101]
MAc-buthylvinyl ether	3.5	6.6	[98]
MAc-hexylvinyl ether	3.5	6.6	[98]

* all the copolymers are described by the authors as 1:1 alternating copolymers
**adding NaCl 0.0092M

group is more acidic and the second one is less acidic, as the comonomer is more hydrophobic. For the copolymers of MAc with different alkenes, the first pK is increased and the second decreased on increasing the number of carbon atoms on the alkyl side chain of the olefinic comonomer. This phenomenon is attributed to an alteration of the effective dielectric constant and its consequent effect on charge-dipole and charge-charge interactions.

MAc copolymers with hydrophobic monomers show potentiometric titration curves with a nonmonotonous dependence of dissociation constant on degree of neutralization, characterized by a maximum and a minimum [84]. This phenomenon is described as a conformational transition and is attributed to the transition from a hypercoiled conformation of the polymer chain at low pH values to a progressively stretched conformation when pH is increased. The hypercoiled conformation "globule" is stabilized by hydrophobic interactions between side chains. The conformational transition is also evidenced by viscometric measurements, dilatometry, calorimetry, and UV absorption spectra.[97-100,102,103]

CONCLUSIONS

The theoretical studies concerning the mechanism of MA copolymerization and the various applications of MA copolymers have required many investigations for their analysis and characterization.

The composition of MA copolymers has been determined by elemental analysis, potentiometric or conductometric titration in organic solvents or their mixtures with water, NMR, IR, UV spectra and from pyrolysis-gas chromatography. The development and improvement of spectroscopic methods, especially ^{13}C NMR spectroscopy, has allowed the estimation of the sequence distribution and generated information about the MA copolymer microstructure. It was found, for example, that MA-styrene copolymer 1:1(moles) contains less than 100% alternating triads. (Semi)quantitative data are also supplied by DSC, based on Tg values, and by PGC, based on the kind and yield of decomposition products.

The molecular weight of MA copolymers has been determined by osmometric, light scattering and viscometric measurements. K and a constants, for use in Mark-Houwink-Sakurada equations, have been determined for a number of MA copolymers. Unperturbed molecular dimensions and steric parameters were estimated from the intrinsic viscosity, using the Stockmayer-

Fixman equation. The rather small values of these parameters could be explained based on the greater flexibility of the copolymer chain due to weakening of the interaction between the side chains separated by the MA units. Size exclusion chromatography is presently the most commonly used method for determining the molecular weight and the molecular weight distribution of these materials. The MW values for some MA copolymers with styrene or methyl vinyl ether fall on an universal calibration curve, demonstrating the validity of universal calibration for these copolymers.

The behavior of aqueous solutions of maleic acid copolymers studied by potentiometric titration, viscometry, calorimetry, dilatometry, UV spectra, and electrical conductivity measurements indicates the two-step dissociation of carboxyl groups. The dissociation constant for the first carboxylic acid group is found in the acid pH domain, while the one of the second carboxylic acid group is found in the basic pH domain, the difference between them being about 3–4 units. This phenomenon is attributed to charge-dipole and charge-charge interactions.

Future investigations regarding maleic copolymers could be centered on the extension of the already used methods to the study of some new MA copolymers or some new MA copolymer derivatives. The analysis and characterization of MA terpolymers, or the study of aqueous solutions of some maleic acid copolymers in which one of the two carboxyl groups was derivatized, would be of interest and could prove useful for the study of the MA terpolymerization mechanism and for the investigation of the role of adjacent groups in the dissociation of maleic polyelectrolytes.

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