

SYNTHESIS AND CHARACTERIZATION OF MALEIC ANHYDRIDE COPOLYMERS AND THEIR DERIVATIVES.
2. NEW DATA ON THE COPOLYMERIZATION OF MALEIC ANHYDRIDE WITH VINYL ACETATE ¹

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The copolymer of maleic anhydride with vinyl acetate has proved good properties as antiscaling agent, soil conditioner, and additive in the leather tanning with chromium basic salts or phosphate substitute in detergents and also suitability as multi-functional material for advanced applications. The molecular mass of the copolymer is a determinant parameter for the application properties. In this paper a systematic investigation regarding the effect of the solvent, monomer concentration, initiator type, and initiator concentration on the molecular mass of MA-VA copolymer is presented. The results are discussed according to the classical theory of the radical copolymerization.

INTRODUCTION

The interest for maleic anhydride (MA) copolymers is continuously growing, due to their successful application in various industrial processes or in medicine and pharmacy.²⁻⁴ Among these the copolymer of MA with vinyl acetate (VA) has proved good properties as antiscaling agent, soil conditioner, additive in the leather tanning or phosphate substitute in detergents.⁵⁻⁸ Recently it evidenced also its suitability as multi-functional material for advanced applications.^{9,10} After the first report on the determination of the copolymerization constants,¹¹ the copolymerization mechanism of MA with VA was extensively studied admitting the charge transfer complex (CTC) participation¹² as the main reason for the formation of 1:1 alternating copolymer. The role of the CTC was confirmed by performing the copolymerization at higher temperatures, when the formation of CTC is hindered and random copolymers could be prepared.¹³ Subsequent studies lined out the role of both CTC and free monomers as polymerization entities.^{14, 15} The studies on the copolymerization required advanced methods of analysis and characterization. The copolymer composition was estimated by conductometric¹⁶ or potentiometric¹⁷ titration and confirmed by IR spectra.¹⁸⁻²⁰ By means of ¹H or ¹³C NMR spectra the alternating character and the microstructure of the copolymer were investigated.^{12b, 21}

The previous studies didn't reported about the molecular mass of this copolymer, which is however a determinant parameter on the physico-chemical behavior and consequently the application of the copolymer, excepted an oversimplified attempt to examine the influence of the polymerization conditions on the copolymer characteristics.²² In this paper a systematic investigation regarding the effect of the solvent, monomer concentration, initiator type, and its concentration on the molecular mass of MA-VA copolymer is presented. Our aim is also to offer detailed data about the possibility to prepare MA-VA copolymers with predicted molecular weight, suitable for different applications.^{5, 23} The results are discussed according to the classical theory of the radical copolymerization.

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EXPERIMENTAL

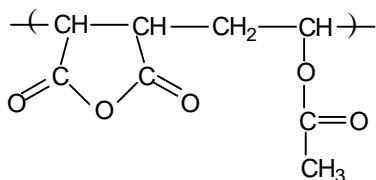
Materials. The monomers, the catalyst, and the solvents were carefully purified before use according to the known methods.^{12b, 24a}

Methods. The MA-VA copolymers were obtained by free-radical copolymerization. The copolymerization reactions were carried out in 100 mL three necked round bottom flasks equipped with a reflux condenser, a thermometer, and a high-speed stirrer and heated in a thermostatted bath. Before polymerization the vessel was flushed with nitrogen and the reaction mixture was also layered with nitrogen. If hydrocarbons or chlorinated hydrocarbons were used as solvent, the copolymer was obtained as a suspension and separated by filtration. If ketones or esters were used, a solution was obtained from which the copolymer was separated by precipitation and filtration. The copolymers were purified by extraction with anhydrous CHCl_3 then dried for 48 h at reduced pressure and 40°C. All the copolymerizations were allowed up to high conversion (80-90%).

The composition of MA-VA copolymer was determined by conductometric titration,¹⁶ with 0.1 N aqueous NaOH in 1:1(vol) acetone: water mixture using a Radiometer CDM210 conductivity meter and a CDC 641T cell. Infrared spectra were recorded on KBr pellet using a Perkin-Elmer 577 Spectrometer. ^1H NMR spectra were recorded on a Cameca TSN 250 MHz spectrometer and ^{13}C spectra were recorded with a Bruker AC 300 MHz spectrometer, both in d_6 -acetone. The average molecular mass (M_V) was estimated by viscometric measurements in acetone at 30 ± 0.1 °C with an Ubbelohde viscometer thermostatted in a water bath. For calculations a Mark-Houwink-Sakurada relation²⁵ was used in which $K = 9.32 \times 10^{-6}$ dL/g and $a = 0.94$.

RESULTS AND DISCUSSION

Copolymer characterization. The copolymer composition was estimated from conductometric titration, being in all cases 50:50 (moles), in the limit of experimental errors. A typical conductometric titration curve in acetone: water mixture is presented in Figure 1. The copolymer structure depicted in Scheme 1 was confirmed by ^1H NMR, ^{13}C NMR and IR spectra.



Scheme 1. Chemical structure of MA-VA copolymer

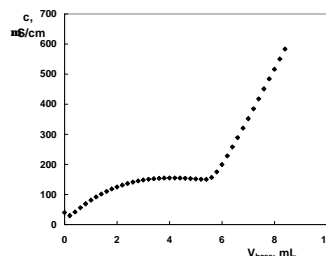


Fig. 1 – Conductometric titration of MA-VA copolymer in acetone-water

Figure 2 (a) and (b) shows respectively ^1H NMR and ^{13}C spectra of a MA-VA copolymer synthesized in benzene. The attribution of the signals according to the literature data^{12b, 12c, 18, 21} is compiled in Table 1 together with characteristic bands of the FTIR spectrum. The ratio of the integrals at 3.5 and 5.7 ppm gives a 1:1 molar composition of the copolymer. The splitting of the signal of methine protons from MA and VA units can be due to the different microenvironment of the two comonomers rather than their non-alternating distribution. It could be also due to a cycloanhydride-enolic tautomerism, according to the recent results of Filimoshkin *et al.*²¹ The signal at 6-7 ppm seem to support this assumption. As seen in Figure 3b, the signal of C=O group from VA is a singlet, that confirm the alternating character of MA-VA copolymer and suggest that the groups have always the same environment along the chain, the dyads MA/VA having the same configuration. The two C=O groups from the MA units have also singlet peaks, evidencing the alternation of the MA and VA units.

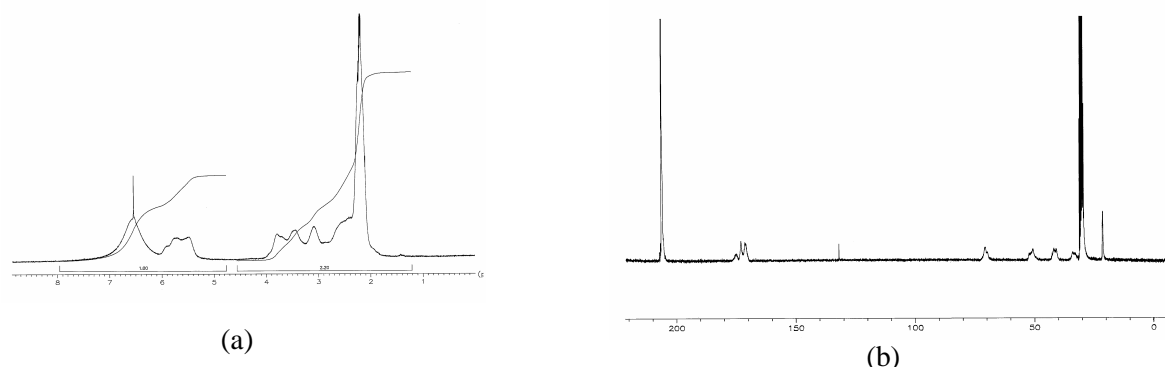


Fig. 2 – The ^1H NMR (a) and ^{13}C NMR (b) spectra of a MA-VA copolymer

Table 1
Typical signals of NMR and FTIR spectra of MA-VA copolymer

	^1H NMR, ppm	^{13}C NMR, ppm	FTIR, cm^{-1}
C = O groups of MA	-	171.5, 170.8	1865, 1784
CH from the MA	large signal centered at 3.5	50.3, 40.6	
C-O-C from MA cycle	-	-	1230, 1095, 1030, 940
C = O groups of VA	-	173.1	1739
CH_3 from the VA	2.00	20.98	
CH_2 from the VA	2.5	32.4	1435, 1380
CH from the VA	peak centered at 5.7	70.6	

Influence of solvent. MA-VA copolymers were obtained by free-radical copolymerization varying the nature of the solvent, the monomer concentration (C_M , grams of monomers in 100 mL mixture), the nature and the concentration of the initiator (C_I , grams of initiator to 100 g monomers). The MA: VA ratio in the feed mixture was 1:1 (moles) in all experiments. Table 2 and 3 present the data regarding the influence of the solvent nature on the molecular mass at different C_M , with high or low amount of benzoyl peroxide (BPO) as initiator. Generally the polymerizations have been performed at the boiling temperature of the solvent which is more convenient for the practice of preparation.

Table 2

The influence of the solvent on the M_V of MA-VA copolymer at different C_M .

Initiator: BPO, $C_I = 2\%$; ^{a)} ϵ : dielectric constant, μ : dipole moment measured in benzene at 20-30°C; ²⁶⁾ ^{b)} the data related to o-xylene are from ref. [24b]; ^{c)} c_S by VA homopolymerization. ^{27b)}

Solvent	t, °C	Reaction time, h	M_V			$\epsilon^{\text{a)}$	$\mu^{\text{a)}$	$10^4 \times c_S^{\text{c)}$
			$C_M, \%$					
			20	14.3	10			
benzene	80	4	38000	32000	21000	2.3	0.0	1.4-3.6
toluene	90	4	14000	8000	7500	2.4	0.4	91.6
xylene ^{b)}	115	4	7000	6000	5000	2.6	0.45	166
chloroform	71	4	26000	21500	19500	4.7	1.1	554
CCl_4	77	4	18000	18000	17000	2.2	0.0	10500
acetone	56	6	15000	14500	14000	20.7	2.7	1.5-12
ethyl acetate	71	6	-	20000	16000	6.0	1.85	7.8

Table 3

The influence of the solvent on the M_V of MA-VA copolymer. $C_M = 25\%$, $C_{\text{BPO}} = 0.2\%$

Solvent	t, °C	Reaction time, h	M_V
acetone	56	6	16000
benzene	80	3	71000
toluene	90	3	40000
xylene	115	4	13000
CHCl_3	71	3	49000

The results show that the nature of the solvent act on the molecular mass of the copolymer, as much as the C_M is higher. It can not be detected a correlation between the M_v and the solvent properties such as dielectric constant or dipole moment. In the case of photoinitiated copolymerization of MA with styrene it was mentioned²⁸ an increase of molecular mass with decreasing of the donor number of the solvent. Some results by MA-VA copolymerization seem to be in accordance with those data, with mention that the reaction temperature was different:

Solvent	Donor number ²⁶	M_v
acetone	17.5	16000
chloroform	0.1	49000

The relatively high molecular mass of the copolymers obtained in solution (acetone, ethyl acetate) are quite surprising, taking into account the well known fact that polymerization in solution gives low molecular polymers.²⁷ This result can be partially attributed to the fractionation procedure of the copolymer by precipitation when the low molecular fractions remain in the mixture solvent-nonsolvent. The influence of the solvent nature on M_v can be correlated with chain transfer reactions between the growing macroradicals and the solvent molecules.^{27a} No data are known regarding the chain transfer to the solvent by MA copolymerization, so we have used the chain transfer constants (c_s) by VA homopolymerization for comparison reasons (Table 2). It can be observed some correlation between the c_s value and M_v : as c_s increases, M_v decreases. The copolymers synthesized in $CHCl_3$ and CCl_4 are excepted, their molecular mass being quite high, even though the chlorinated solvents are known as polymerization regulators due to their high c_s value.

Influence of monomer concentration. Figure 3 shows the influence of C_M on M_v of MA-VA copolymer. An increase of molecular mass is observed when C_M increases, according with the general equation of free radical polymerization.^{27a} In the case of the copolymerization in benzene with 0.25% BPO the results are setting on a straight line that passes through the origin, which could suggests no chain transfer in this case even tough the polymerization was not stopped at low conversion. In the case of MA-VA copolymer the values of M_n and M_v are quite close (unpublished data).

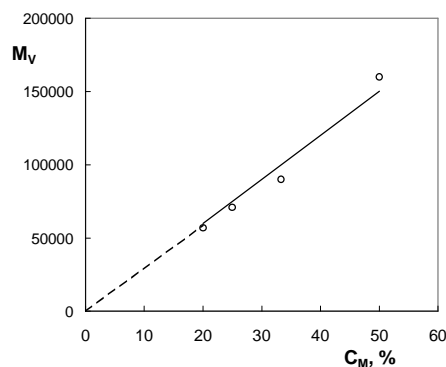


Fig. 3 – The C_M influence on M_v of MA-VA copolymers obtained in benzene. Initiator: BPO, $C_i = 0.25\%$

Influence of the nature and concentration of the initiator. Table 4 shows the influence of the initiator on M_v of MA-VA copolymer obtained in benzene or toluene. Three radical initiators were used, namely benzoyl peroxide, lauroyl peroxide (LPO) and 2,2'-azobisisobutyronitrile (AIBN). It can be observed that even if the decomposition temperature and rate of the initiators are relatively close,^{27c} the molecular mass of MA-VA copolymers obtained with BPO are higher that those obtain in the presence of AIBN or LPO. This behavior can be correlated with different efficiency of the initiators. It can be admitted that for a period of time the radicals resulted by the initiator decomposition are close to each other like in a “cage” of

Table 4

The influence of the initiator nature on the molecular mass of MA-VA copolymer obtained in benzene or toluene. $C_M = 25\%$. Reaction time: 4 h

Solvent	Initiator (I)	C_I , %	t, °C	M_V
benzene	AIBN	0.20	80	45000
benzene	BPO	0.20	80	75000
benzene	LPO	0.20	80	49000
toluene	AIBN	3.0	90	11000
toluene	BPO	3.0	90	19000

solvent molecules. A part of the radicals recombines themselves and just a low amount of them diffuse and initiate the polymerization. The fraction of free radicals that takes part in the polymerization initiation is related to the efficiency of the initiator.^{27d} The influence of the BPO concentration by the copolymerization of MA with VA in benzene or toluene is shown in Table 5 and 6, respectively.

Table 5

The influence of C_I on the M_V of MA-VA copolymer obtained in benzene, with BPO, at 80°C, reaction time 4 h

C_{BPO} , %	$C_{BPO}^{1/2}$	M_V	
		C_M , %	
		25	20
0.11	0.33	89000	-
0.25	0.50	104000	58000
0.50	0.71	73000	51000
1.0	1.00	44000	-
1.5	1.22	-	40000

Table 6

The influence of C_I on the M_V of MA-VA copolymer obtained in toluene, with BPO, at 80°C, reaction time 5 h

C_{BPO} , %	$C_{BPO}^{1/2}$	M_V		
		C_M , %		
		20	14.3	10
0.5	0.71	17000	-	-
1.0	1.0	16000	9000	8000
1.5	1.22	17000	-	-
2.0	1.41	14000	8000	7500
3.0	1.73	13000	-	-
5.0	2.24	12000	8000	6000

The results show that C_I influence on the molecular mass is more evident when C_M is higher. The molecular mass decreases when C_I , respectively $C_I^{1/2}$ increase, excepted the very small concentration of initiator ($C_I < 0.2\%$). These results can be understood by considering one of classical equations of free radical polymerization:^{26a}

$$\frac{1}{GP} = \frac{(k_{tc}/2 + k_{td}) \cdot V_i^{1/2}}{(k_{tc} + k_{td})^{1/2} \cdot k_p [M]} + \frac{k_{fm}}{k_p} + \frac{k_{fs} [S]}{k_p [M]} + \frac{k_{fc} [I]}{k_p [M]} \quad (1)$$

in which: GP – the number average degree of polymerization; k_{tc} – the rate coefficient for termination by combination; k_{td} – the rate coefficient for termination by disproportionation; V_i – the initiation rate; k_p – the rate coefficient for propagation; k_{fm} – the rate coefficient for transfer to monomer; k_{fs} – the rate coefficient for transfer to solvent; k_{fc} – the rate coefficient for transfer to initiator; $[M]$ – the concentration of monomer; $[S]$ – the concentration of solvent; $[I]$ – the concentration of initiator.

If we take into account that by small initiator concentration the chain transfer to initiator can be neglected,^{27a} the equation (1) becomes:

$$\frac{1}{GP} = \frac{(k_{ic}/2 + k_{td}) \cdot V_i^{1/2}}{(k_{ic} + k_{td})^{1/2} \cdot k_p [M]} + \frac{k_{fm}}{k_p} + \frac{k_{fs} [S]}{k_p [M]} \quad (2)$$

It can be speculated that, at small concentration of initiator, the first term of the right in the equation (2) becomes very small, but the terms that show the chain transfer have a quite high value, so that at low C_I values the molecular mass is also low. After our knowledge such behavior was not yet observed by MA copolymerization.

Another possibility to obtain MA-VA copolymers with high molecular mass is to replace partially or totally the solvent with an excess of VA, taking into consideration that usually $k_{fm}/k_p \ll k_{fs}/k_p$. Table 7 shows the results by MA copolymerization with VA in benzene (Bz), VA or Bz + VA mixtures. The results seem to confirm that $k_{fm} < k_{fs}$. The presence of an excess of VA can lead to the VA homopolymerization as side reaction. Taking into account this possibility, all samples in Table 7 were purified by reprecipitation from acetone, which is a good solvent for both copolymer and poly(vinyl acetate), in benzene, which precipitate only the copolymer.

Table 7

The influence of the reaction medium composition on the molecular mass of MA-VA copolymer. Initiator: POB, $C_I = 0.2\%$. Reaction time: 4 h. * excepted the VA used as comonomer, according to the recipe

Solvent	VA fraction in the solvent, % vol*	C_M , %	t, °C	M_V
Bz	0	25	80	98000
Bz + AV	25	25	80	91500
Bz + AV	33	25	80	123500
Bz + AV	50	25	80	213500
Bz + AV	75	25	80	245000
AV	100	10	73	319000

CONCLUSION

The main parameters that influence the molecular mass by MA copolymerization with VA are: the solvent nature, the monomer concentration and the initiator nature and concentration. These parameters influence the molecular mass according to the traditional radical copolymerization theory, but some peculiarities can be attributed to the specific mechanism of copolymerization with the participation of CTC. In order to obtain MA-VA copolymers with high molecular mass, the copolymerization of MA with VA in 1:1 (moles) ratio is suited, using benzene as solvent and BPO as initiator. The partial substitution of benzene with VA leads to an important increase of the molecular mass.

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