

*Dedicated to Professor Ionel Haiduc
on the occasion of his 70th anniversary*

SYNTHESIS AND CHARACTERIZATION OF MALEIC ANHYDRIDE COPOLYMERS AND THEIR DERIVATIVES. 3

SYNTHESIS AND CHARACTERIZATION OF MALEIC ANHYDRIDE - METHYL METHACRYLATE COPOLYMERS^{1,2}

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The radical copolymerization of maleic anhydride with methyl methacrylate is one of examples in which the charge transfer complex between the monomers is less involved, so that the copolymers are differing from 1:1 (moles) composition. In our contribution the effect of the solvent, monomer concentration, initiator type and concentration on the composition and molar mass of maleic anhydride-methyl methacrylate copolymer was systematically examined, aiming to obtain copolymers with composition close to 1:1 (moles) and the molar mass relatively high. The copolymers were characterized by conductometric titration, FTIR and ¹H NMR spectra, while the thermal behavior was examined by thermogravimetric analysis and differential scanning calorimetry.

INTRODUCTION

Maleic anhydride copolymers are largely used, firstly in biomedical applications,³ but also as antiscaling agents, phosphate substitutes in detergent compositions, dispersants, flocculants, soil conditioners.⁴ They hydrolyze in water giving carboxylic polyelectrolytes, whose behavior in aqueous solution is governed mainly by electrostatic interactions between polyions and counterions. This behavior is also influenced by the structural characteristics of maleic acid copolymers, such as the presence of two neighboring carboxylic groups in the maleic units, the hydrophilic/hydrophobic character of the comonomer, the polymer conformation. All these effects contribute to some particular features of maleic acid polyelectrolytes: the two-step dissociation, the typical binding of counterions, conformational transitions induced by pH variation.

Maleic acid – methyl methacrylate copolymers, obtained from maleic anhydride (MA)-methyl methacrylate (MMA) copolymers, have proved efficient as crystal growth modulators or corrosion inhibitors.^{5,6} Among maleic anhydride/acid copolymers having generally a 1:1 (moles) composition, the copolymers with methyl methacrylate are differing from 1:1 composition, which can provide specific properties related to the hydrophobic character.⁷ The copolymerization of MA with MMA was studied in what concerns the mechanism of copolymerization and the characterization of the copolymers by NMR and IR spectra.⁸ The literature data outline a particular copolymerization behavior of this pair of comonomers compared to other systems involving MA. The copolymerization constant r_1 is close to 0, no matter the solvent in which the copolymerization is performed. The r_2 constant depends on the solvent, its value lying between 0.9 and 4.63.^{4a} The amount of MA in the copolymers is lower than that

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corresponding to the molar ratio 1:1, so that the MA-MMA copolymers are soluble in solvents such as benzene, toluene, etc, in which most of MA alternating copolymers are insoluble.⁹ The copolymerization data have been explained using the classical terminal model, the penultimate model or the CTC model, depending mainly on the solvent and initiator type.^{8,10,11} The copolymerization of MA with other methacrylates such as tetradecyl methacrylate, tert-butyl methacrylate or trimethylsilyl methacrylate evidenced the same tendency to form non-alternating copolymers.^{12,13} It is to mention that the MA-MMA are quite biocompatible, being examined for bone cement formulations in combination with hydroxyapatite¹⁴ or derivatized with disinfecting agents.¹⁵

The experiments presented in this paper have been aiming to obtain copolymers having the composition close to 1:1 (moles) and the molar mass relatively high. In this purpose a series of copolymerization reactions have been performed varying the solvent, the monomer concentration, the nature and concentration of the initiator. The copolymers were characterized using the methods given in the literature¹⁶ or adapted to this copolymer.¹⁷

EXPERIMENTAL PART

Materials. The monomers, the catalysts, and the solvents were carefully purified before use according to the known methods.^{18,19}

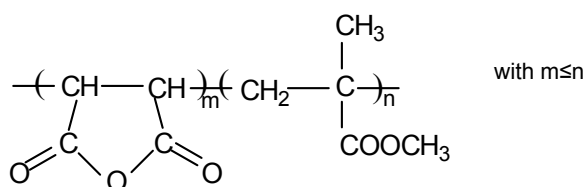
Methods. The MA-MMA copolymers were obtained by free-radical copolymerization. The copolymerization reactions

were carried out in vessels flushed with nitrogen, the reaction mixture being also layered with nitrogen. The polymerizations have been performed in solution and the copolymers have been recovered by precipitation in diethyl ether followed by purification by repeated washing with diethyl ether : petroleum ether mixture and drying for 48 h at 40°C and reduced pressure.

The composition was determined by conductometric titration¹⁷ with 0.1 N aqueous NaOH in 1:1(vol) acetone: water mixture using a Radiometer CDM210 conductivity meter and a CDC 641T cell. FTIR spectra were recorded on KBr pellet using a Vertex 70 Bruker Spectrometer and ¹H NMR spectra were recorded on a Cameca TSN 250 MHz spectrometer in *d*₆-acetone. The average molar mass (*M_v*) was estimated by viscometric measurements in acetone at 30±0.1 °C with an Ubbelohde viscometer.¹⁶ The thermooxidative decomposition under dynamic conditions of heating has been performed with a Paulik-Paulik-Erdey Derivatograph MOM-Budapest on 50 mg samples, at 12°C/min. Differential scanning calorimetry analysis was performed with a Pyris Diamond DSC - Perkin Elmer instrument.

RESULTS AND DISCUSSION

Most maleic anhydride copolymers have a 1:1 (moles) composition and a regular, alternating structure, mainly due to the large participation of a charge transfer complex (CTC) formed by the comonomers before polymerization. Unlike that, in the copolymerization of MA with MMA the CTC is less involved^{8,10} so that the composition is different from 1:1 (moles), as shown in Scheme 1. For this reason we focused firstly on the copolymer characterization regarding the composition by conductometric titration, and spectrometric investigation by ¹H NMR and FTIR method.



Scheme 1 – Chemical structure of maleic anhydride-methyl methacrylate copolymer.

Copolymer characterization. An example of conductometric titration curve of MA-MMA copolymer having the composition MA:MMA=1:2.60 (moles) is given in Figure 1. The titration curve exhibits a typical shape similar to other MA copolymers^{2,8} in which the end point can be easily estimated.

In the ¹H RMN spectrum presented in Figure 2 it can be observed the peak at 3.8 ppm ascribed to the protons of –COOCH₃ group and the large

signal at 1-2 ppm attributed to the α protons –CH₃ in MMA units.⁸ The peak centered at 3.4 ppm can be attributed to the maleic protons, the signal from the CH₂ group protons being probably located in the range 2.5-3.0 ppm. In the poly(methyl methacrylate) spectrum, the signal from α –CH₃ is split in three peaks at 1.01; 1.08 and 1.20 ppm, due to the syndiotactic, heterotactic and isotactic configuration, respectively. Cazé *et al.*⁸ found, for the MA-MMA copolymer, the same signal split at

1.14; 1.20 and 1.24 ppm. In our case, this signal is split in three peaks, at 1.08; 1.38 and 1.6 ppm, possibly due to the presence of sequences of several MMA units with different configurations. Because the signal of the maleic protons is not well resolved, the estimation of the copolymer composition is not possible. The peak at 6.5 ppm comes from residual maleic acid. The broad signal centered at 5.3 ppm could result from a cycloanhydride-enolic tautomerism mentioned for other MA copolymers.^{2,20,21}

The FTIR spectrum of a MA-MMA copolymer with MA: MMA=1:2.60 (moles), presented in Figure 3, confirms the information from the NMR spectrum. The characteristic bands of the anhydride cycles can be noticed at 1860, 1784 cm^{-1} (C=O) and 1090, 941 cm^{-1} (C–O–C). The band at 1728 cm^{-1} is characteristic to the C=O from ester groups of MMA units. The broad band at 1246 cm^{-1}

results from C–O–C bonds of anhydride cycles as well as from C–O bonds of ester groups. The bands at 1443 and 1379 cm^{-1} are due to the deformation vibrations of the CH_2 groups. The signals at 1150 and 1443 cm^{-1} , assigned to some sequences of more than three units of MMA²², are in agreement with the copolymer composition and the peaks in the NMR spectra.

The influence of solvent. Table 1 gathers the results regarding the composition and molecular mass of the MA-MMA copolymers obtained in different solvents. The reaction yields were between 60 and 70%, but these values are not relevant because almost all copolymerizations proceeded in solution and the polymers were recovered by precipitation. It is known that the polymeric species with lower molar mass could remain in the solvent-nonsolvent system.

Fig. 1 – Conductometric titration curve of an MA-MMA copolymer.

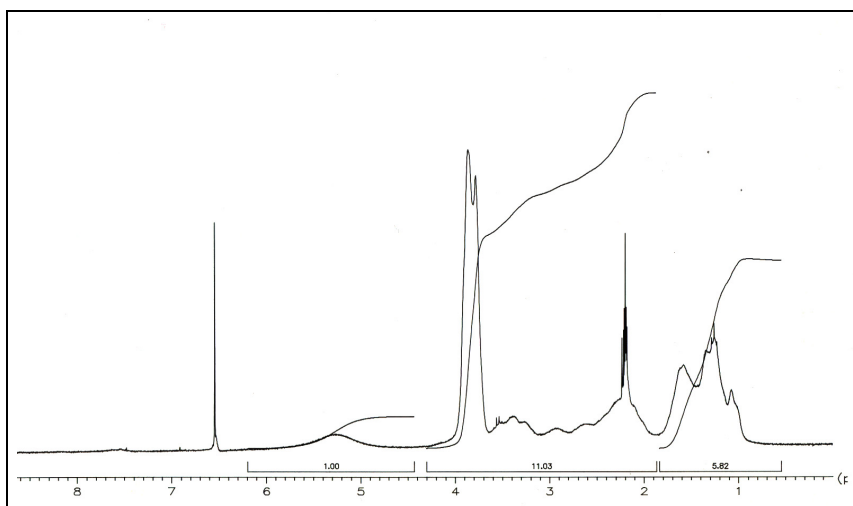
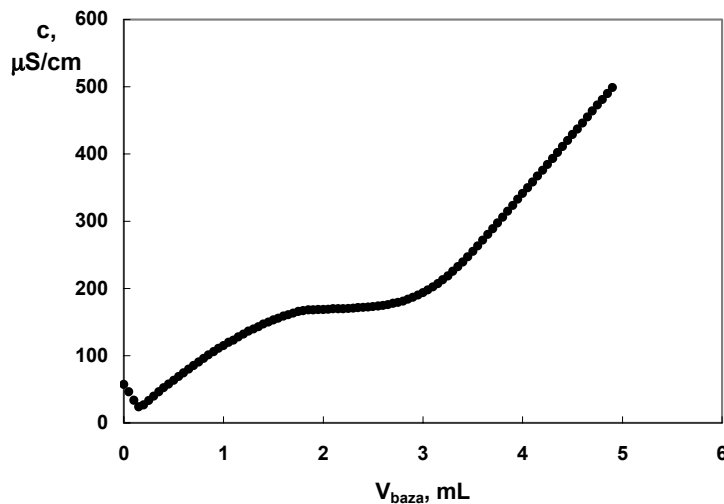


Fig. 2 – ^1H NMR spectrum of the MA-MMA copolymer recorded at 250 MHz.

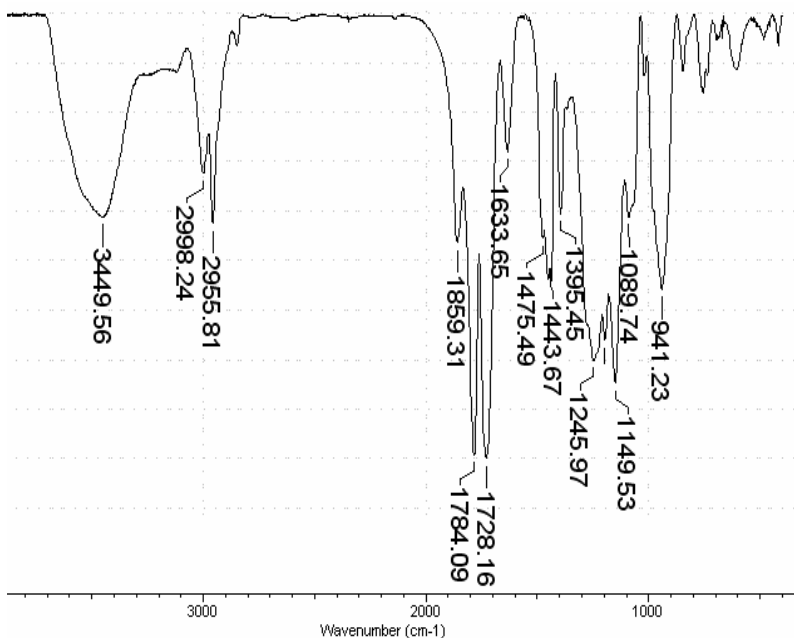


Fig. 3 – FTIR spectrum of MA-MMA copolymer.

Table 1

The influence of the solvent upon the composition and the molar mass of the MA-MMA copolymer. MA:MMA ratio= 1:1 (moles); $C_M=50$ g/dL; initiator: benzoyl peroxide (BPO); reaction time: 8 hours

Solvent	Dielectric constant	C_{BPO} , %	t , °	MA:MMA ratio in copolymer (moles)	M_v^*
Dichloroethane	10.4	0.5	80	1:1.34	32000
Acetone	20.7	1.0	56	1:1.44	38000
Acetonitrile	37.5	1.0	80	1:1.53	40000
Dioxane	2.2	0.5	80	1:3.04	43000
Cyclohexanone	18.3	0.5	80	1:1.49	54500
Ethyl acetate	6.0	0.5	77	1:1.91	71000
Butyl acetate	-	0.5	80	1:2.38	-
2-butanone	18.5	0.5	80	1:1.52	48500

* In literature there are data concerning the determination of molar mass using the Mark-Houwink-Sakurada equation with $K=12.4 \times 10^{-5}$ dL/g and $a=0.69$. These values must be used with caution because the composition range for which the data are recognized was not specified.¹⁶

It can be observed that the copolymers synthesized in solvents with a higher dielectric constant have a composition closer to 1:1(moles). This suggests that, by the solution copolymerization the charge transfer complex (CTC) between the two comonomers does not play an important role,

in accordance to the results obtained by other authors.^{8,10}

The influence of the monomer concentration. (C_M) on the molar mass of the MA-MMA copolymer synthesized in 2-butanone is presented in Table 2.

Table 2

The influence of C_M on the molar mass of the MA-MMA copolymers synthesized in 2-butanone. Initiator: BPO; $C_{BPO}=1\%$; MA : MMA ratio= 1:1(moles); temperature: 80°C; reaction time: 8 hours

C_M , g/100mL	Molecular mass*	MA:MMA ratio in the copolymer(moles)
100	47000	1:1,52
50	33000	1:1,49
33,3	21500	1:1,48
20	18500	1:1,58

* See Table 1

The influence of the initiator. Table 3 presents the **influence** of the initiator nature and concentration on the molar mass of the MA-MMA copolymer obtained in 2-butanone. Three radical

initiators were used, namely BPO, 2,2'-azobisisobutyronitrile (AIBN) and lauroyl peroxide (LPO).

Table 3

The influence of the nature and concentration of the initiator to the molecular mass of the MA-MMA copolymer. Solvent: 2-butanone; MA-MMA ratio = 1:1(moles); C_1 – initiator concentration, g/100g monomers; temperature: 80°C; reaction time = 8 hours

Initiator	C_1 , %	C_M , g/100mL	M_v^*
BPO	0,5	100	54500
BPO	1,0	100	47000
AIBN	0,5	100	38000
AIBN	1,0	100	31000
LPO	1,0	100	25500
BPO	0,5	50	37000
BPO	1,0	50	33000
AIBN	0,5	50	38500
AIBN	1,0	50	22000

* See Table 1

In the case of MA-MMA copolymerization, the nature and concentration of the initiator influence in a relatively small extent the molar mass of the copolymers. The values vary not so much, between 22000 and 54500. However, it can be noticed that the highest M_v values are obtained by using the BPO as an initiator. The monomer and initiator concentration influences on the M_v in a qualitative accordance with the radical polymerization theory that is, M_v increases with the increase of the monomers concentration and decreases with the increase of the initiator concentration.

Stage	Temperature range, °C	T_m , °C	Weight loss, %
I	30-100	76	0.6
II	100-240	145	5.2
III	240-440	344	80
IV	440-560	528	11.2

The first decomposition stage can be assigned to the loss of moisture from the copolymer, the amount of absorbed water being relatively low, in accordance to the hydrophobic character of the MMA. The second step can be due to the loss of chemically bound water, when the eventually hydrolyzed MA units are transformed in anhydride cycles. The third stage of decomposition, between 240 and 440°C corresponds to an important loss of weight – 80% – and could be mainly due to the depolymerization of the MMA small blocks (of course, this assertion should be confirmed by

Thermal characterization of the copolymers.

The thermal behavior was analysed by thermogravimetric analysis and differential scanning calorimetry, in order to get useful information for the further applications, e.g. as membrane precursors or partner for composite materials. Figure 4 presents the thermogram of the MA-MMA copolymer having the composition MA: MMA=1:2.60 (moles). The decomposition takes place in several stages, as following (T_m is the temperature corresponding to the maximum rate of weight loss):

means of additional methods). The decomposition takes place up to the almost complete degradation of the copolymer (97%). It is to be noticed the accordance of our results regarding the main steps of decomposition II and III with the results of Bhuyan and Dass.²³

Figure 5 presents the DSC diagram of the MA-MMA copolymer having the composition MA : MMA=1:2.60 (moles). Glass transition temperature T_g is 125°C, lower than those of the alternating copolymers of MA with vinyl acetate or styrene.²⁴

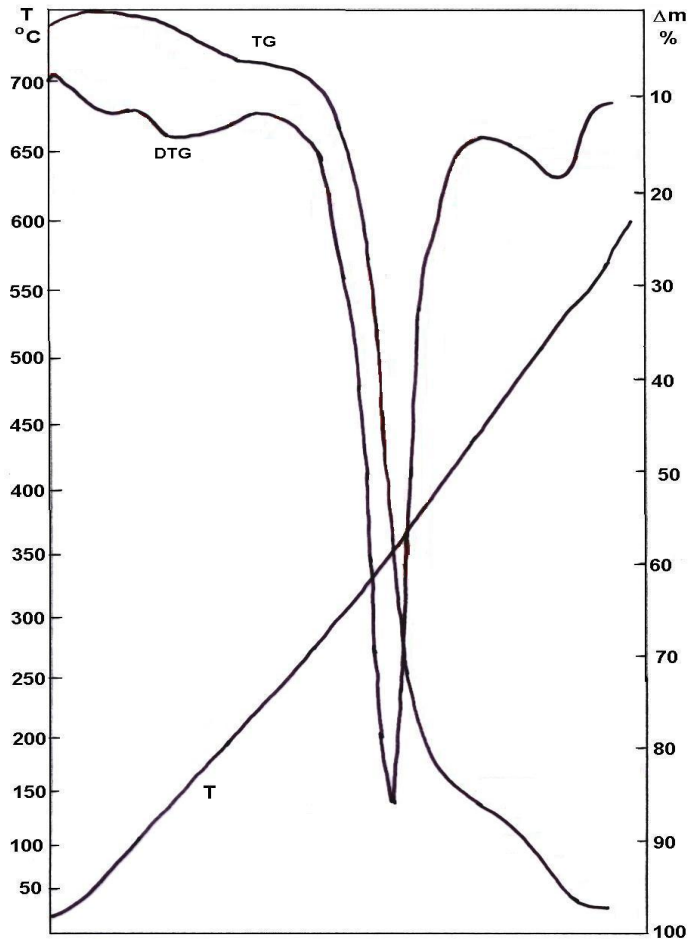


Fig. 4 – The thermogram of MA-MMA copolymer.

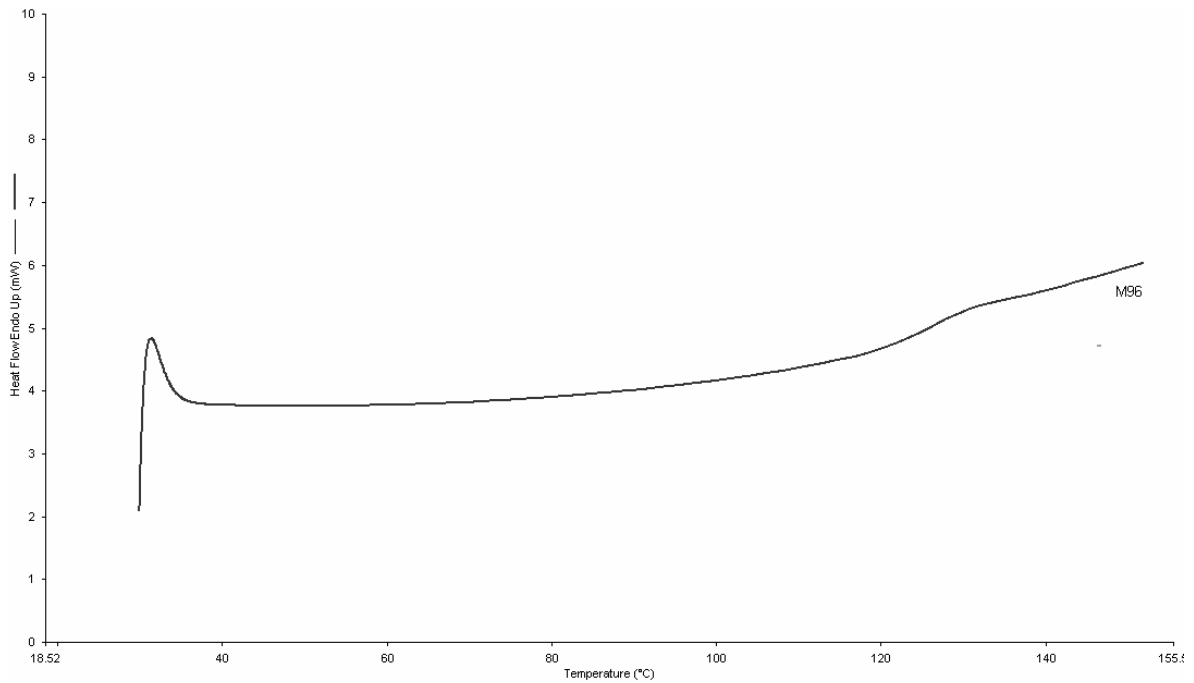


Fig. 5 – The DSC diagram of the MA-MAM copolymer.

CONCLUSION

The experiments for the obtaining of the MA copolymers with MMA have evidenced the influence of the solvent on the copolymer composition in a way that confirms the reduced participation of the CTC in the copolymerization reaction. The monomer concentration, the nature and concentration of the initiator influence the molar mass of the copolymer in a smaller extent than in other MA copolymerizations. In order to obtain copolymers having the composition closer to the 1:1 ratio and the molar mass as high as possible, it is recommended to perform the copolymerization of the MA with MMA in a molar ratio of 1:1(moles) using 2-butanone or cyclohexanone as solvent, higher monomer concentration and BPO as initiator.²⁵

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