

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

### 4. SYNTHESIS AND CHARACTERIZATION OF MALEIC ANHYDRIDE-ACRYLONITRILE COPOLYMERS<sup>1,2,3</sup>

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The copolymers of maleic acid with acrylonitrile can be applied in the fabrication of membranes for ultrafiltration, pervaporation and enzyme-immobilization. In this paper we present new results on the synthesis of maleic anhydride-acrylonitrile copolymer by radical copolymerization in organic solvents. We have examined the effect of the synthesis conditions: solvent, monomer ratio, and monomer concentration on the composition and molar mass of the copolymer. The composition of copolymers was determined by different methods: elemental analysis, conductometric titration in water/organic media, titration in nonaqueous medium, FTIR and <sup>1</sup>H NMR spectra. The data were compared and the most reliable and convenient method was identified.

#### INTRODUCTION

Polyacrylonitrile-based materials are used for membrane fabrication due to their excellent film-forming character. Copolymerization of acrylonitrile (AN) with maleic anhydride (MA), a hydrophilic monomer, has been performed to improve the hydrophilicity and antifouling property of acrylonitrile-based polymeric membranes. Maleic acid-AN copolymers have been used in the ultrafiltration membranes<sup>4</sup> or pervaporative membranes for dehydration of 1-methoxy propanol.<sup>5</sup> Maleic acid-AN copolymers are better than poly(acrylonitrile) for the fabrication of membranes for pervaporative separation of polar solvent from polar-nonpolar mixture because MA interacts with the polar solvent. Thus, pervaporative membranes for methanol separation from methanol-benzene mixture<sup>6</sup> or methanol-toluene mixture<sup>7</sup> have been prepared. The -COOH groups in the membrane form a secondary (hydrogen) bond with methanol and methanol sorption increases by increasing the number of these groups.

The structure and performance of acrylonitrile copolymer membrane are influenced by the casting

conditions,<sup>8</sup> by the post-treatment of the membrane (thermal treatment and base treatment),<sup>9</sup> and by the molar mass of the copolymer.<sup>10</sup> Ultrafiltration membranes of MA-AN copolymer can successfully immobilize enzymes, even if the MA content in the copolymer is very low.<sup>11</sup> The anhydride groups from the MA-AN copolymer membranes can be reacted with poly(ethylene glycol) for improving antifouling property and biocompatibility.<sup>12</sup>

Previous works evidenced that the reactivity ratio  $r_1$  (corresponding to MA) is close to 0, no matter the solvent in which the copolymerization is performed. The  $r_2$  (corresponding to AN) reactivity ratio depends on the solvent, its value lying between 2.23 and 7.7, thus the amount of MA in the copolymers is much lower than that corresponding to the molar ratio 1:1 usual for many maleic anhydride copolymers.<sup>13</sup> Abel *et al.* studied free-radical copolymerization of MA with AN in solution (N,N-dimethylformamide, N,N-dimethylacetamide,  $\gamma$ -butyrolactone, ethylene carbonate), by precipitation polymerization (dioxane) or bulk polymerization and found that in all cases, the content of maleic anhydride in the polymers did not exceed 5 mol-%.<sup>11</sup> Copolymerization of

MA with AN was also performed by a water-phase precipitation copolymerization process with  $K_2S_2O_8$ - $Na_2SO_3$  as redox initiator system<sup>4</sup> or by emulsion polymerization with  $(NH_4)_2S_2O_8$ - $Na_2SO_3$  as initiator<sup>5</sup> when maleic acid-AN copolymers were obtained. In both cases, the MA mole fractions in the copolymer are low (between 3 and 22%).

Our work has been aiming to obtain copolymers having a high MA content and a higher molar mass as well as the systematic characterization of the MA-AN copolymers. In this purpose a series of copolymerization experiments have been performed varying the solvent, the monomer ratio, and the monomer concentration. The copolymers were characterized regarding their composition by elemental analysis, different titration methods, FTIR and <sup>1</sup>H NMR spectra, while the molar mass was estimated by means of intrinsic viscosity values obtained from viscometric measurements in N-methylpyrrolidone.

## EXPERIMENTAL

**Materials** MA was purified by recrystallization from chloroform.<sup>14</sup> AN was purified by vacuum distillation. The initiators were recrystallized by usual procedure, and the solvents were also carefully purified before use.<sup>15</sup>

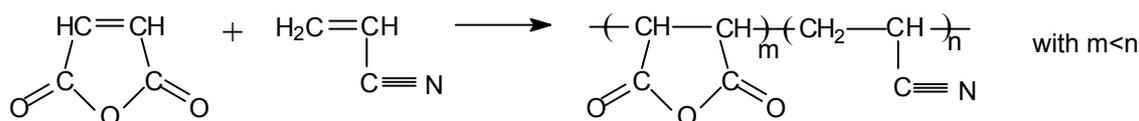
**Synthesis** The MA-AN copolymers were obtained by free-radical copolymerization performed in solution-suspension using benzene, 1,4-dioxane, chloroform or acetonitrile as solvents, or in solution using N,N-dimethylacetamide. The copolymers obtained as suspensions were recovered by

filtration, and then purified by repeated washing with diethyl ether and dried at reduced pressure and 40°C for 48 h. When the copolymer was obtained in solution, it was precipitated in diethyl ether, and then purified as before. The MA-AN copolymers are light yellowish powders, soluble in N,N-dimethylformamide, N,N-dimethylacetamide (DMA), dimethylsulfoxide or N-methyl-2-pyrrolidone (NMP). They are not soluble in acetone, dioxane, chloroform, acetonitrile, benzene, water or aq. NaOH.

**Characterization** The copolymer composition was determined by various methods. Elemental analysis was performed using a CHNS/O Analyzer Perkin Elmer 2400 Series II. The conductometric titration was performed with 0.1 N aqueous NaOH in 1:1(vol) organic solvent: water mixture using a Radiometer CDM210 conductivity meter and a CDC 641T cell, by adapting the method proposed by Cazé *et al.*<sup>16</sup> Another method was the titration in nonaqueous medium according to the method proposed by Brown and Fujimori.<sup>17</sup> FTIR spectra were recorded on KBr pellet using a Vertex 70 Bruker spectrometer and the <sup>1</sup>H NMR spectra were recorded on a Bruker Avance DRX 400 NMR spectrometer in *d*<sub>6</sub>-DMSO. The intrinsic viscosity was determined by viscometric measurements in NMP at 30±0.1 °C with an Ubbelohde viscometer. By our knowledge, there are no data in the literature on the *K* and *a* constants from Mark-Houwink-Sakurada equation. Anyway, taking into account the variable and different from 1:1 moles composition of AM-AN copolymers the comparison of the copolymers only by their intrinsic viscosity [ $\eta$ ] seems more reliable than some molar mass calculations.

## RESULTS AND DISCUSSION

The copolymerization of MA with AN proceeds as presented in Scheme 1.



Scheme 1 – Copolymerization of maleic anhydride with acrylonitrile.

**Copolymer characterization** In our previous works<sup>2,3</sup> regarding the synthesis and characterization of MA copolymers with vinyl acetate or methyl methacrylate we adapted for composition determination the conductometric titration proposed in the literature,<sup>16</sup> the solvent being a 1:1 (vol) mixture acetone: water. As the MA-AN copolymers are not soluble in acetone, we chose as solvent a 1:1 (vol) mixture NMP: water, but the titration curve is rather smooth, as it can be seen in Fig. 1.

Another method was the composition evaluation from FTIR spectra. The quantitative

analysis of MA copolymers by means of FTIR spectra was already proposed. Thus, it was estimated the composition of MA terpolymers<sup>20</sup> or of MA copolymers derivatives.<sup>21</sup> The FTIR spectrum of a MA-AN copolymer (Fig. 2) exhibits the expected characteristic bands of the C=O groups of MA units at 1850 and 1782  $cm^{-1}$  and the characteristic bands for C-O-C from the anhydride cycles at 1239, 1060, 970 and 940  $cm^{-1}$ . The band at 2244  $cm^{-1}$  is due to -CN stretching vibration of AN,<sup>5</sup> and the band at 1453  $cm^{-1}$  corresponds to CH<sub>2</sub> and CH groups.

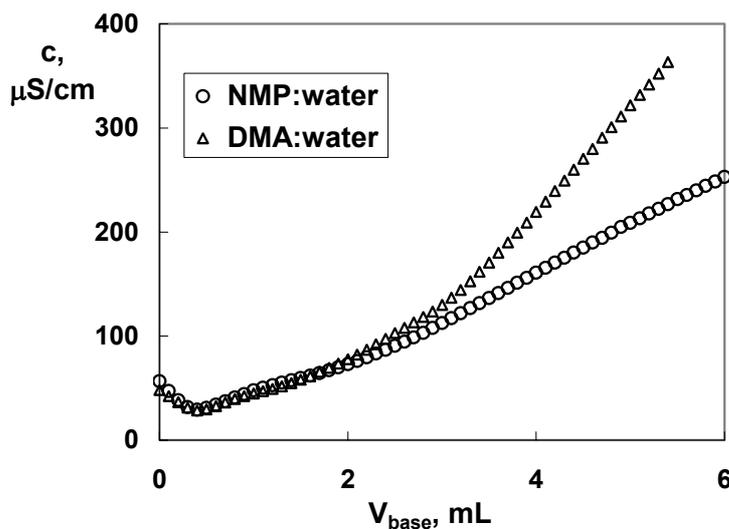


Fig. 1 – The conductometric titration curve of an AM-AN copolymer in NMP:water and in DMA:water mixture.

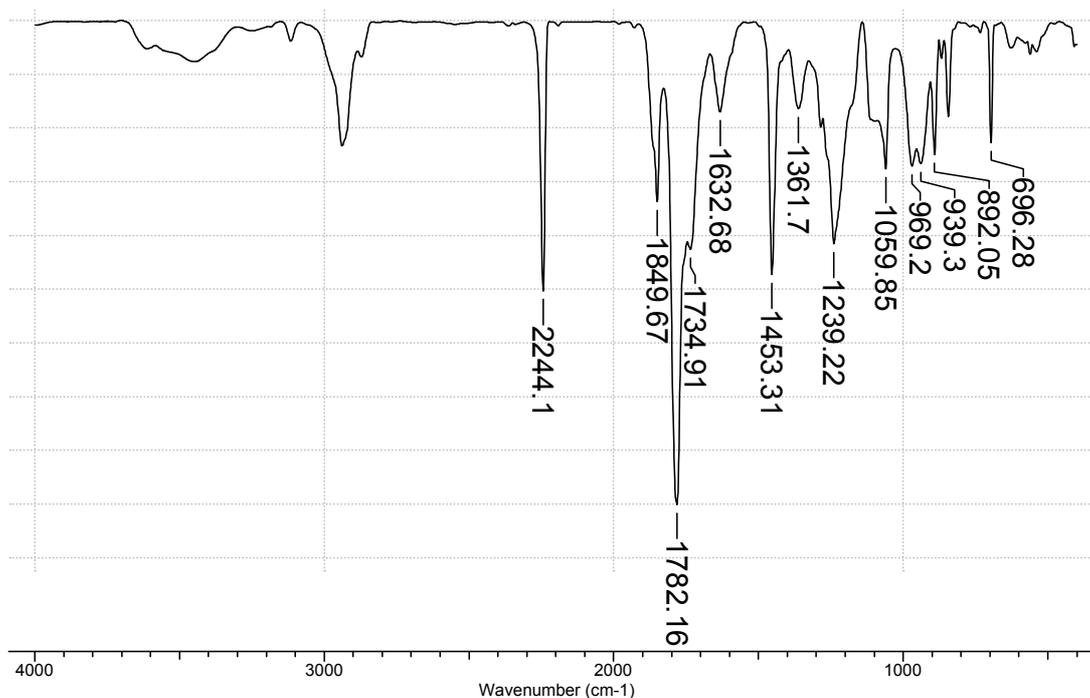


Fig. 2 – The FTIR spectrum of MA-AN copolymer.

The copolymer composition was determined using the Lambert-Beer law according to the equations:

$$v_1 : A_{AN} = \alpha_{AN} \cdot b \cdot X_{AN}$$

$$v_2 : A_{MA} = \alpha_{MA} \cdot b \cdot X_{MA}$$

where:  $v_1$  – wave number of a specific band of AN monomer which do not overlap with any band of MA ( $2230 \text{ cm}^{-1}$ ),  $v_2$  - wave number of a specific band of MA monomer which do not overlap with any band of AN ( $1783 \text{ cm}^{-1}$ ),  $A_{AN}$  and  $A_{MA}$  – the

areas of the absorption bands of AN and MA,  $\alpha$  - a proportionality constant, analogue to the absorptivity from the Lambert – Beer law,  $b$  – path length of the sample,  $X_{AN}$ ,  $X_{MA}$  - mass fractions of corresponding monomers.

$$\frac{A_{AN}}{A_{MA}} = \frac{\alpha_{AN} \cdot b \cdot X_{AN}}{\alpha_{MA} \cdot b \cdot X_{MA}} = \frac{\alpha_{AN}}{\alpha_{MA}} \cdot \frac{X_{AN}}{1 - X_{AN}}$$

The  $A_{AN}/A_{MA}$  ratio was calculated from the calibration set recorded on various monomer

mixtures in NMP. The slope  $\alpha_{AN}/\alpha_{AM}$  was determined by plotting the ratio  $A_{AN}/A_{MA}$  against  $X_{AN}/(1-X_{AN})$ .  $X_{AN}$  for a given copolymer was estimated using this ratio and the  $A_{AN}/A_{MA}$  from the spectrum.

Actually, in the literature were described several methods for the composition determination of MA copolymers, including the conductometric titration of copolymers dissolved in acetone/water with aqueous NaOH,<sup>16</sup> the reaction of anhydride groups with aniline and titration in organic medium of the formed monoacid with ethanolic NaOH (Brown-Fujimori method),<sup>17</sup> the conversion of anhydride groups with n-butylamine and back-titration of unreacted amine with HClO<sub>4</sub> in glacial acetic acid,<sup>18</sup> the complete hydrolysis of anhydride

groups and titration of acid groups with aqueous NaOH or the reaction of anhydride groups with p-chloroaniline followed by Cl-determination after the Schöniger-decomposition.<sup>11,19</sup> We applied some of these methods in order to find the most suitable method to characterize our copolymers. The first choice was to change the solvent in the conductometric titration, so a DMA:water mixture 1:1 (vol) was used. From Figure 1 presented above it can be observed that the inflection point on the titration curve in DMA:water mixture is much better evidenced than in the case of NMP:water. To confirm these results, elemental analysis of the nitrogen content and the titration after Brown-Fujimori method were also performed and the results are collected in Table 1.

Table 1

Comparison between copolymer compositions determined by different methods

Method for the composition determination	Copolymer composition, MA:AN (moles)	
	N18 sample	N20 sample
Conductometric titration in NMP:water mixture	1:5.4	1:7
Conductometric titration in DMA:water mixture	1:6.0	1:5.5
FT-IR spectroscopy	1:8.0	1:7.7
Titration in nonaqueous medium	1:5.1	1:5.4
Elemental analysis of N	1:4.1	1:4.2

The better accordance is observed between the results of conductometric titration and Brown-Fujimori method. The nitrogen analysis give a lower content of AN, respectively a higher content of MA explainable by the fact that often this analysis on polymers is not reliable. FTIR method led to the determination of a smaller content of MA compared to titration; it can be because only unhydrolyzed MA cycles are analyzed by this method. It is to be mentioned that generally the potentiometric titration of maleic acid copolymers is subjected to some errors connected to their chemical structure. The two carboxylic groups of each maleic acid unit are not equivalent, one of them being strong, the other weak.<sup>22</sup> It was demonstrated that, depending on the nature of the comonomer and the titration conditions, only one or both acidic groups can be measured.<sup>23</sup> So the conductometric titration in DMA:water mixture seems the most reliable and convenient method for the determination of the MA-AN composition.

The <sup>1</sup>H NMR spectrum of the MA-AN copolymer, shown in Fig. 3, confirms the copolymer structure. The peak centered at 3.3 - 4.0 ppm can be attributed to the maleic protons CH. The large signal centered at 2.05 ppm can be ascribed to the protons of CH<sub>2</sub> group in AN units

and the signal at about 3.15 ppm is attributed to the protons CH in acrylonitrile units, similarly to the spectra of an acrylonitrile-methacrylic acid copolymer.<sup>24</sup> The peak at 6.4 ppm could result from the maleic acid traces present in the copolymer.

*The influence of solvent* MA-AN copolymers were obtained by free-radical copolymerization changing the solvent and maintaining constant the monomer concentration  $C_M$  (mol/L), the monomer ratio and the concentration of the initiator  $C_I$  (grams of initiator to 100 g monomers). Table 2 gathers the results regarding the composition and intrinsic viscosity of the MA-AN copolymers obtained in different solvents. It can be observed that the copolymers have the composition between 1:4 and 1:7.5 (MA:AN) and the values of intrinsic viscosity are mainly in the range 0.2-0.3 dL/g. Different results were obtained in acetonitrile, when the intrinsic viscosity was as high as 0.526 dL/g and the highest yield was attained. The copolymerization of this pair of comonomers proceeds not by the usual alternating mechanism, like for the other copolymers of MA, so it can be supposed a different solvation of the monomers or macroradicals.

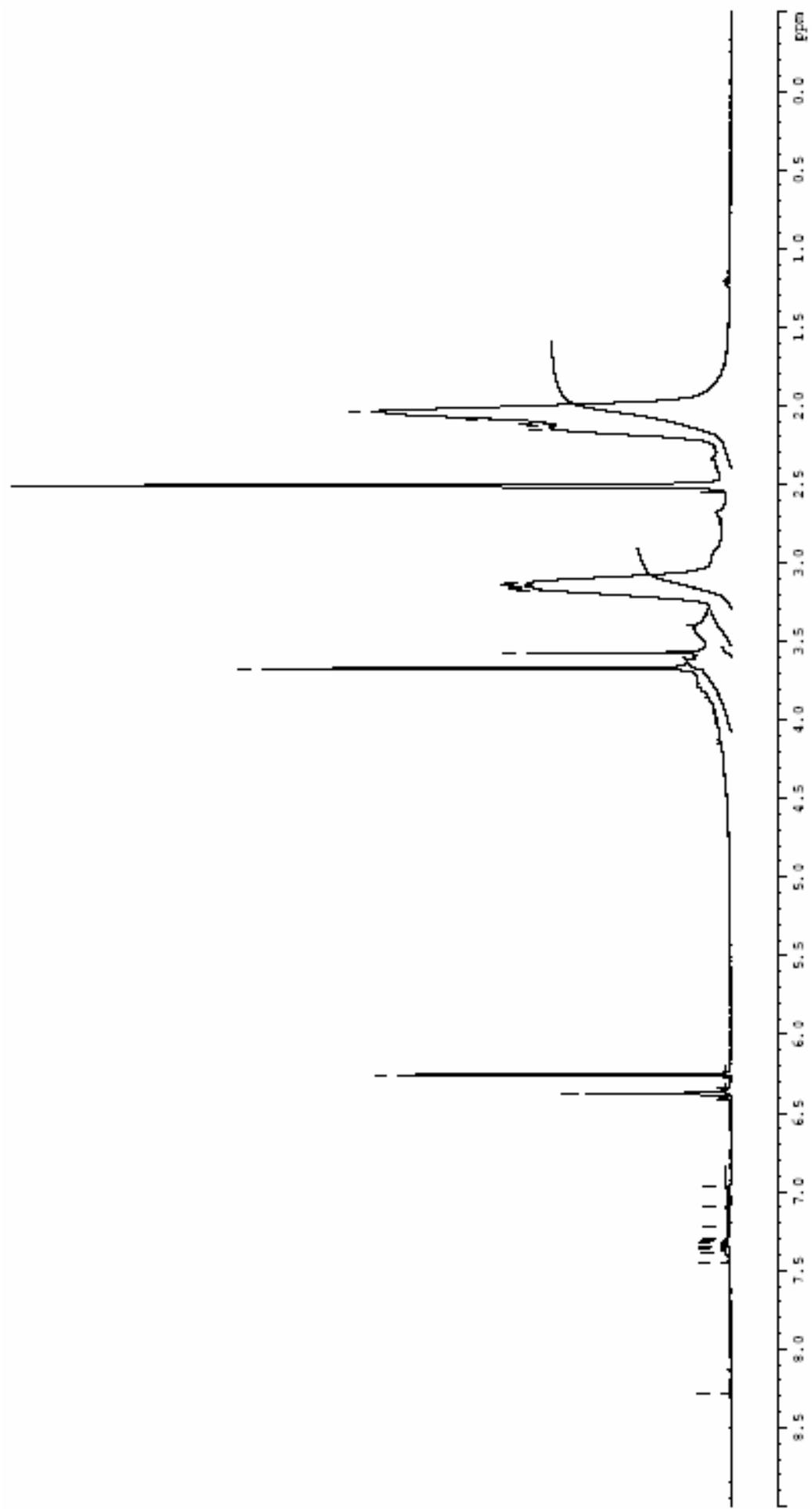


Fig. 3 –  $^1\text{H}$  NMR spectrum of the MA-AN copolymer recorded at 400 MHz.

Table 2

The influence of the solvent upon the composition and the intrinsic viscosity of the MA-AN copolymer. MA:AN ratio= 1:1 (moles);  $C_M=9.24$  mol/L, initiator: BPO,  $C_I=0.5\%$ ; duration 6 h, temperature  $80^\circ\text{C}$

Solvent	Yield, %	MA:AN ratio in copolymer (moles)	$[\eta]$ (dL/g)
Benzene	11	1:5	0,262
Dioxane	13.5	1:5.5	0.280
Chloroform	7,8	1:7.5	0.246
Acetonitrile	19	1:6.3	0.526
N, N -dimethylacetamide	5.7	1:4.5	-

The influence of the monomer concentration on the composition and intrinsic viscosity of the MA-AN copolymer synthesized in benzene and dioxane is presented in Table 3. The intrinsic viscosity decrease as the monomer concentration is lower, which would be in accordance with the classical polymerization theory. It is observed a variation of the copolymer composition at the same MA:AN ratio in the feed, which could be explained also by

the different solvation of the monomers or macroradicals. Otherwise, according to the composition different from 1:1 (moles) and taking into account the reluctance of MA to the homopolymerization, the MA-AN copolymers would contain units of MA separated by sequences of several AN units. So, the intrinsic viscosity can be influenced not only by the molar mass, but also by the composition.

Table 3

The influence of  $C_M$  on the composition and intrinsic viscosity of the MA-AN copolymers. Initiator: BPO;  $C_I=0.5\%$ ; MA:AN ratio= 1:1(moles); temperature  $80^\circ\text{C}$ ; duration 6 h

Solvent	$C_M$ , mol/L	Yield, %	MA:AN ratio in copolymer (moles)	$[\eta]$ (dL/g)
Benzene	9.24	11	1:5	0.262
	5.44	9.1	1:3	-
	3.86	9.7	1:6.9	0.149
Dioxane	9.24	13.5	1:5.5	0.280
	5.44	13	1:7.8	0.262
	3.86	7.9	1:10	0.209

The influence of the monomer ratio in the monomer feed on the composition and intrinsic viscosity of the MA-AN copolymer synthesized in benzene and dioxane is presented in Table 4. As

expected, the amount of MA in the copolymer increases with the increasing of MA amount in the monomer feed.

Table 4

The influence of the of the monomers ratio in the monomer feed on the composition and intrinsic viscosity of the MA-AN copolymers.  $C_M=9.24$  mol/L, initiator: BPO;  $C_I=0.5\%$ , temperature  $80^\circ\text{C}$ ; duration 6 h

Solvent	MA:AN (moles)	Yield, %	MA:AN ratio in copolymer (moles)	$[\eta]$ (dL/g)
Benzene	1:1	11	1:5	0,262
	2:1	6,7	1:5	-
	3:1	4.2	1:4	-
Dioxane	1:1	13.5	1:5.5	0.280
	2:1	5.7	1:3	0.173
	3:1	2.8	1:3	-

The reaction yield is relatively low and the MA content in the copolymers is rather low, between 8.5 and 25 % moles, in accordance with the literature data.<sup>4,5,12</sup> To improve this performance, other methods of copolymerization could be suitable, as for example radical controlled polymerization (ATPR).

## CONCLUSION

The copolymerization of maleic anhydride with acrylonitrile has been investigated regarding the effect of the synthesis conditions such as solvent, monomer ratio, and monomer concentration on the composition and molar mass of the polymers. The

composition of the copolymers was determined by different methods: elemental analysis, conductometric titration in water/organic media, titration in nonaqueous medium, FTIR spectra. The conductometric titration with aqueous NaOH using a mixture N, N- dimethylacetamide:water 1:1 (vol) as solvent is recommended as the most convenient and reliable. The RMN and FTIR spectra confirmed the chemical structure of the copolymer.

The monomer concentration and the monomer ratio in the reaction feed have a rather poor influence on the copolymer composition and intrinsic viscosity. In order to obtain copolymers having higher amount of maleic anhydride and molar mass (intrinsic viscosity) it is recommended to perform the copolymerization of the maleic anhydride with acrylonitrile in a molar ratio of 1:1 (moles) using dioxane or acetonitrile as solvent, higher monomer concentration and benzoyl peroxide as initiator.

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