# CHEMICAL TRANSFORMATION OF POLY(STYRENE-ALT-MALEIC ANHYDRIDE) WITH *p*-AMINO-N, N-DIETHYLANILINE

Roxana BADULESCU,[a] Ion BOLOCAN[a*] and Dan Sorin VASILESCU[b]

[a] Oil and Gas University, Faculty of Petroleum Research and Petrochemistry, Department of Organic Chemistry,
39 bdv. Bucureşti, Ploiesti, Roumania
[b] Politehnica University, Faculty of Applied Chemistry and Material Science, Department of Polymer Science and Technology,
149 Calea Victoriei, Bucharest, Roumania

Poly (styrene-alt-maleic anhydride) may be conveniently used as an intermediate in preparing functional polymers, since compounds containing amino or hydroxy groups can be linked to this copolymer via ring-opening reactions. In this study, the chemical transformation of poly (styrene-alt-maleic anhydride) with *p*-amino-N,N-diethylaniline is described. The kinetic of amidation, in acetone and dimethylformamide has been studied, considering only the first step of the conversion to acid amides. The structure of amidated copolymer has been confirmed by FTIR, UV-Vis, H[1]-NMR, TGA and DSC methods.

## INTRODUCTION

Acid anhydrides easily react with aromatic amines, even in the absence of catalysts; as the temperature increases, different compounds are to be obtained, following the order ammonium salt, amides and imides.[1,2] The same pattern is prevailing for succinic units present on a polymer chain, as in the alternating poly(styrene-alt-maleic anhydride) (SMA); obviously, the reaction rate would be lower in such chemical transformations, due to the restrained access of aromatic amine toward the succinic unit.[3-5]

The versatility and diversity of the resulted products (mixtures consisting in salt, amide, diamide, and imide) is shown by numerous applications such as dispersing agent[6] or coatings.[7] The nature of reactants, their molecular weights, as well as the solvent used in reaction influence conversion. Increasing the basicity of aromatic amine (corroborated with lack of any steric hindrance) results in growth of the reaction rate;[6,8] we have already reported this feature.[9,10]

The present work describes the non-catalytic amidation of SMA with *p*-amino-N,N-diethylaniline (PADEA).

## EXPERIMENTAL

**Materials.** SMA has been obtained according to the data from literature;[11] its molecular weight (viscometry in tetrahydrofurane – THF) was found as being around 13000. We have used $k=5.07 \cdot 10^{-3}$ ml/g and $\alpha=0.81$, solvent toluene, $T=30$ ℃, according to literature data.[12] The amines and solvents used (acetone, dimethylformamide - DMF) and PADEA (Merck) have been used as such.

**Chemical transformation of SMA.** Amidation took place in anhydrous solvents, either at room temperature, or at 50-55℃, under vigorous stirring; the reaction product has been precipitated into a suitable non-solvent, filtered and dried under vacuum. All samples have been washed with 20-30 ml from the suitable non-solvent (petroleum ether when working in acetone and HCl 20% for the samples resulted in DMF). Even if it is quite unusual to use two different non-solvents, in practice it has been proved (after using several non-solvents) that our choice seems to be optimal. Once the filtrate became colorless, we have subsequently washed again this time with ethyl ether. The presence of unreacted amine in filtrate has been proved by FTIR.

As the conversion (with respect to PADEA) has been appreciated by weight measurements, it implied the quantitative separation of samples from the reaction mixture, followed by careful extraction of un-reacted PADEA. Presuming that the amidation reaction is governed by a second order kinetics, the rate constant is given by:

$$k = \frac{2.303}{t\left(c_{0a} - c_{0b}\right)} \cdot \lg\left[\frac{c_{ob}\left(c_{0a} - c\right)}{c_{0a}\left(c_{0b} - c\right)}\right] \qquad (1)$$

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* Corresponding author: ibolocan@upg_ploiesti.ro

where *c* represents anhydride concentration after a given time t, while $c_{0a}$ and $c_{0b}$ are the initial concentrations of amine and anhydride, respectively. Provided that the condition $c_0a=c_0b=c_0$ is obeyed, then:

$$\frac{1}{c}=\frac{1}{c_o}+kt \qquad (2)$$

In the above equation the slope is the rate constant[13] to be calculated.

The products obtained have been characterized by infrared spectroscopy (FTIR), using a Nicolet Avatar 360 apparatus; the samples were prepared for ATR technique. UV spectra were recorded on a Jasco 550V spectrophotometer; the samples were dissolved in DMF. ¹H-NMR spectra were recorded on a Varian Gemini 300 apparatus; dimethylsulphoxide (DMSO) has been used as solvent -$d_6$ (3.34 and 2.51 ppm). Thermal properties of products have been investigated by TGA and DSC; a DuPont 2100 apparatus

(heating rate 20ºC/minute) has been used for this purpose. DSC analysis has been carried out under a nitrogen cushion.

## RESULTS AND DISCUSSION

The reaction between SMA and PADEA has been performed in acetone at room temperature and also in DMF at 50ºC. Table 1 presents the reaction conditions as well as the conversions reached. It has been noticed that in acetone, a ceiling is reached after 24 hours. When working in DMF, at room temperature, the conversions obtained were quite small; the result at 40 % has been reached at a far higher initial concentration (see last row in Table 1), and also upon heating.

*Table 1*

Reaction of SMA with PADEA

| Solvent | Ratio of the initial molar concentrations anhydride/amine | Reaction time (hours) | Conversion with respect to amine, (%) | The ratio of peak intensities (1776cm⁻¹/704 cm⁻¹) |
|---|---|---|---|---|
| Acetone (Petroleum ether used for precipitation) | 0.05/0.05 | 0,5<br>3<br>7<br>24<br>48 | 1<br>25<br>40<br>42<br>42 | 4,2<br>1,6<br>1,4<br>1,3<br>1,0 |
| DMF (HCl 20% used for precipitation) | 0.05/0.05* | 24 | 10 | 1,3 |
| | 0.83/0.2** | 2<br>3<br>4 | 22<br>32<br>40 | 3,8<br>1,5<br>0,38 |

\* at room temperature; \*\* at 50 ºC

Based on the data presented in Table 1, we have calculated the rate constant for amidation of SMA with PADEA in acetone (see Fig. 1).
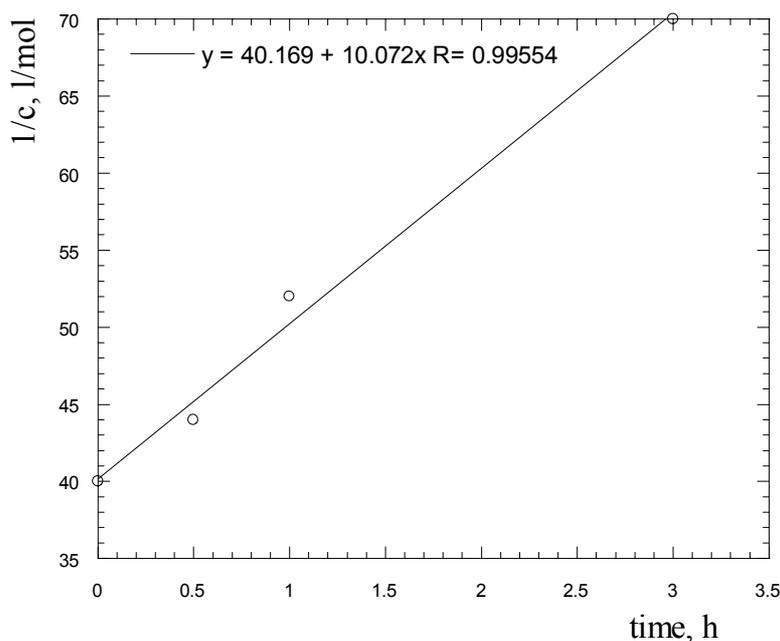


Fig. 1 – Reaction kinetic for the reaction between SMA and PADEA in acetone at room temperature.

Experiments carried out by Rätzsch[14] about amidation of SMA with p-substituted anilines at 45° C have shown increases in reaction rate up to 30 times, when acetone has been used as solvent. Our tests [9,10] have shown that the rate constant in the reaction of SMA with PADEA in acetone as solvent (room temperature) is only three times higher, than that recorded when working in DMF at 50°C. Carrying out the reaction in acetone under heating does not represent a workable solution, as the polymer and amine form "a slurry" after 30 minutes of heating.

The modified copolymers were further characterized by FTIR, UV, $^1$H-NMR spectroscopy and thermal analysis. The corresponding FTIR spectra of SMA/PADEA products, obtained in acetone and DMF, respectively, are presented in figure 2; the initial molar ratio was 1/1, and the reactants have been mixed 24 hours at room temperature. The decrease in the intensity of the peak at 1776 cm$^{-1}$ could be attributed to the reacted anhydride towards ammonium salt, amide and even imide.[15-18]

Reaction yield may be appreciated by the decrease of the ratio of peaks due to anhydride, with respect to a peak remaining constant throughout the whole reaction time;[19,20] such a referential peak might be that corresponding to the monosubstituted aromatic ring at 700cm$^{-1}$ (see table 1). According to literature data [20] the peak situated at 1715 cm$^{-1}$ is characteristic to imide function. For both solvents the absorption ratio [1776 cm$^{-1}$]/[704 cm$^{-1}$] decreases in time; in DMF the ratio becomes 0.38 (anhydride reacts in a greater amount), while in acetone, this ratio remains higher than 1.0). The decrease of the intensity ratio 1776 cm$^{-1}$/704 cm$^{-1}$ might also be due to a partial hydrolization of the anhydride ring; such a phenomenon is not unusual, being, for instance reported by Shulkin, [21] this time during synthesis in 'anhydrous' solvents.
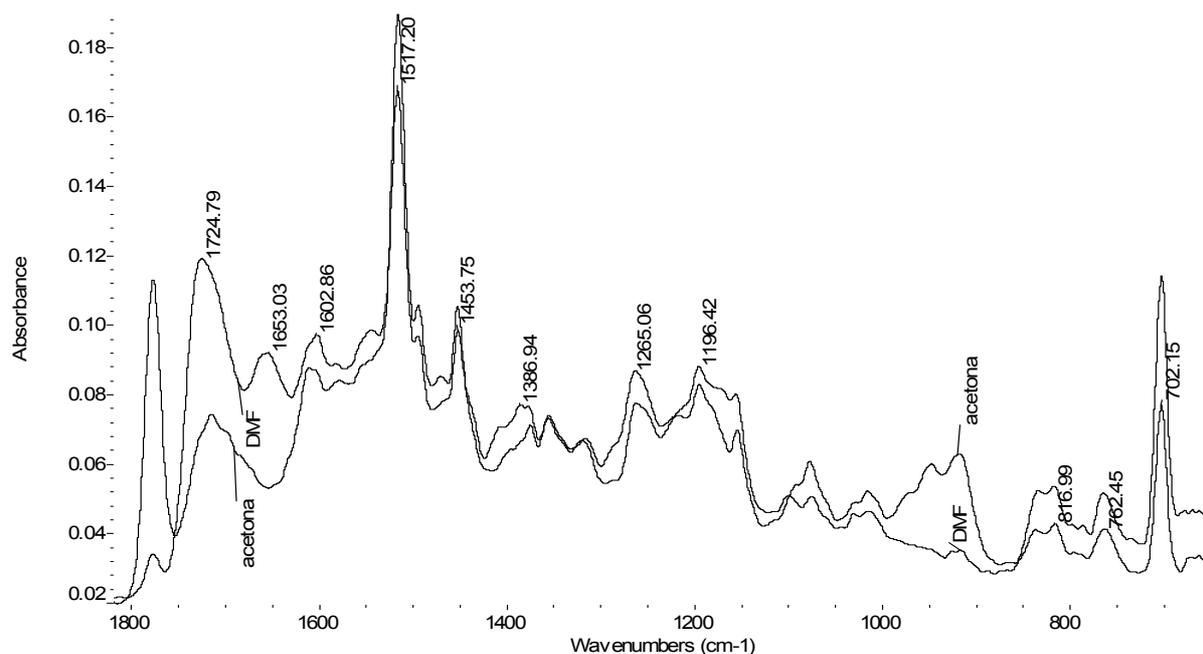


Fig. 2 – FTIR spectra of the reaction products of SMA with PADEA obtained in acetone and DMF, respectively.

It may be noticed that amide peaks I and II (1650 cm$^{-1}$ and 1540 cm$^{-1}$) are better solved when working in DMF; also, when carrying out the reaction in acetone as solvent, an important amount from the anhydride repeat units of copolymer remains unreacted. This assertion is supported by the difference in peak areas at 850-1000 cm$^{-1}$, region customarily attributed to the function C-O-C in anhydride. Moreover, FTIR analysis brings supplementary information regarding the amount of reacted amine. Thus, the intensity of the peak situated at 1517 cm$^{-1}$ (aromatic ring of amine) may be correlated with that placed at 700 cm$^{-1}$. The value of this ratio is 1.8 when working in acetone, but 2.5 when the reaction has been carried out in DMF; accordingly, it may be said that in DMF, the amount of reacted amine is higher, in comparison with the use of acetone. Obviously, this evaluation has to be associated with a complete removal of unreacted amine; the fact is to be certified by UV analysis (lack of absorption at ~330 nm).

Fig. 3 illustrates (in the same graph) the UV spectra for SMA, PADEA and the reaction product (after 48 hours of reaction, at room temperature, in acetone), respectively.

As shown in Fig. 3, the UV spectrum of the reaction product exhibits a broad absorption centered at 283 nm. Spectral superpositions resulting in a large peak may be decomposed by deconvolution technique,[22-23] provided by the software included in the Jasco apparatus. However, this method has been used only for qualitative analysis of spectra. Consequently, in the spectrum of the reaction product, an amidation compound ($\lambda_{max}$ at 286 nm) might be identified (Fig. 4).
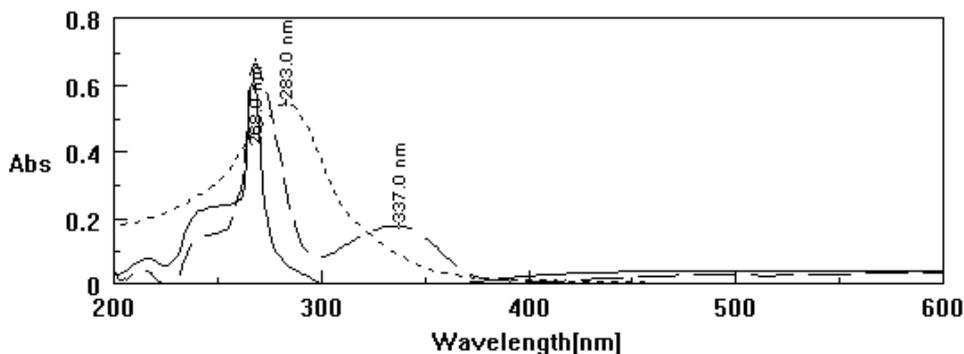


Fig. 3 – Superposition of UV spectra: (___)SMA, (- - -)PADEA and (…) SMA+PADEA;
(All spectra recorded in DMF at concentrations of $4,7\cdot10^{-3}$, $1,52\cdot10^{-4}$ and $6,58\cdot10^{-4}$ mol copolymer unit/l).
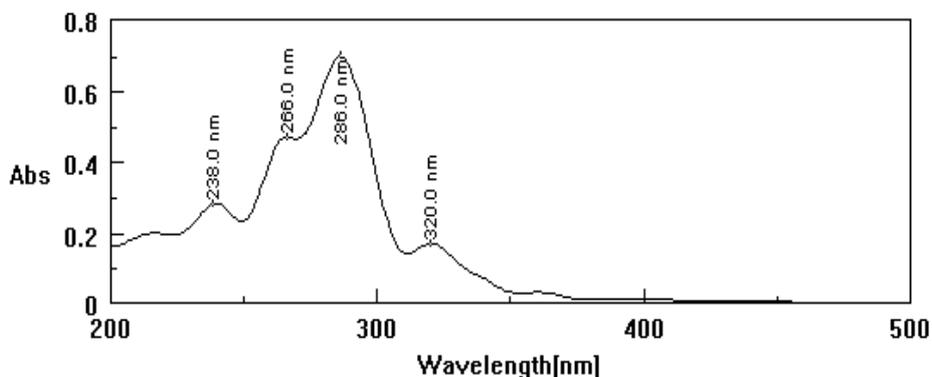


Fig. 4 – UV spectrum (deconvolution) for the reaction product of SMA with PADEA
(DMF as solvent; $c = 6,58\cdot10^{-4}$ mol copolymer unit/l).

The general feature of UV spectra of the reaction product does not change as a function of reaction time. In this respect, we have superposed the spectra of obtained polymers (reaction time in the range 0.5 – 24 hours, in acetone, see Fig. 5); spectra have been recorded in DMF at concentrations between 4.3 and $8.5\cdot10^{-5}$ mol/L. In all situations we have noticed an absorption at 282 nm, accompanied by a shoulder at 267 nm; however, the molar extinction coefficients (at 282 nm) increase from 7500 to 11000 l/mol·cm, as the reaction time increases as well. For SMA modified with PADEA we have calculated the extinction coefficients with respect to the repeat unit. Also, we have obtained the molar extinction coefficients for the initial SMA at 268 nm (200 L/mol·cm) and PADEA at 267 nm (approx 10 000 L/mol·cm) and 338 nm (1600 L/mol·cm), respectively.

We have also noticed this unusual behaviour and we think that besides amides, an important amount of ammonium salt has been formed when working in acetone. In turn, the salt precipitates forming a slurry. When carrying out the reaction of SMA with PADEA in acetone, at room temperature, we have noticed the appearance of a precipitate; as the conversion increases, the nature of repeating units change, and consequently the copolymer solubility.

According to FTIR analysis,[24] amidation with PADEA takes place at larger conversion, when working in DMF, in comparison with acetone (Fig. 6); obviously, this fact can be easily explained by the different concentrations used (higher in the case of DMF). On the other hand, when carrying out the reaction at room temperature, an important amount of ammonium salt is formed.

Accordingly, when working in acetone, besides the polyamic acid, a significant quantity of ammonium salt is withheld, resulting in an apparent increase of conversion.

The reaction progress has also been put into evidence by recording the corresponding NMR spectra. For instance, in $^1$H-NMR spectrum of SMA/PADEA, in acetone, after 12 hours, the following peaks (Fig. 7) may be noticed: 6,7-7,6 and 6,2-6,7 ppm (aromatic protons either from styrenic units, or from amine), 6 ppm (presumably, due to the amidic proton), 1,2-1,3 (s) ppm and 0,9-1,2 (q) ppm (aliphatic protons from $-C_2H_5$, or the main chain).
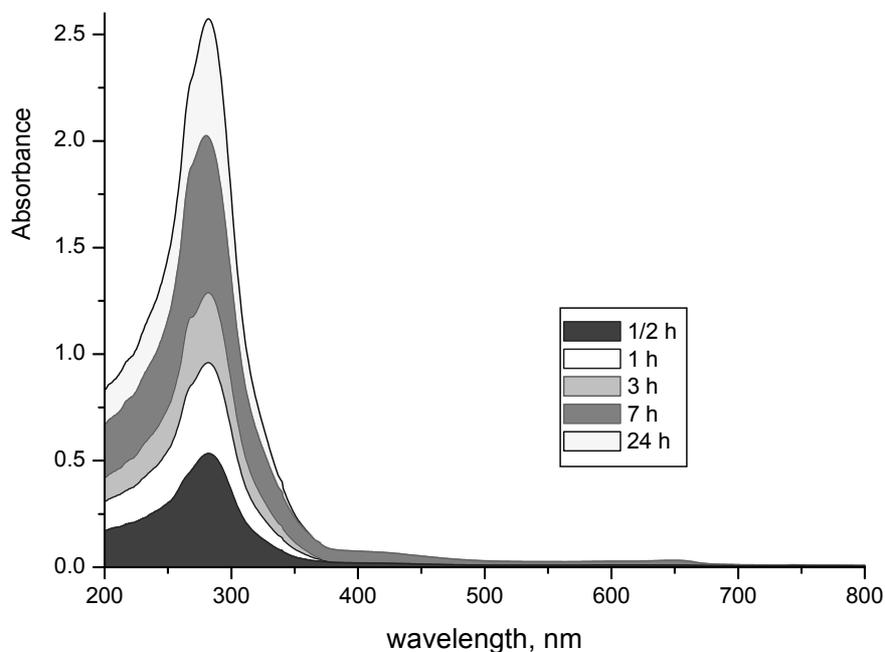


Fig. 5 – Superposition of UV spectra, of the reaction product (SMA/PADEA) obtained in acetone after 1/2, 1, 3, 7 and 24 respectively; spectra have been recorded in DMF at the following concentrations: $4,37 \cdot 10^{-5}$, $5,11 \cdot 10^{-5}$, $8,57 \cdot 10^{-5}$, $7,26 \cdot 10^{-5}$ and $5,25 \cdot 10^{-5}$ mol copolymer unit/l).
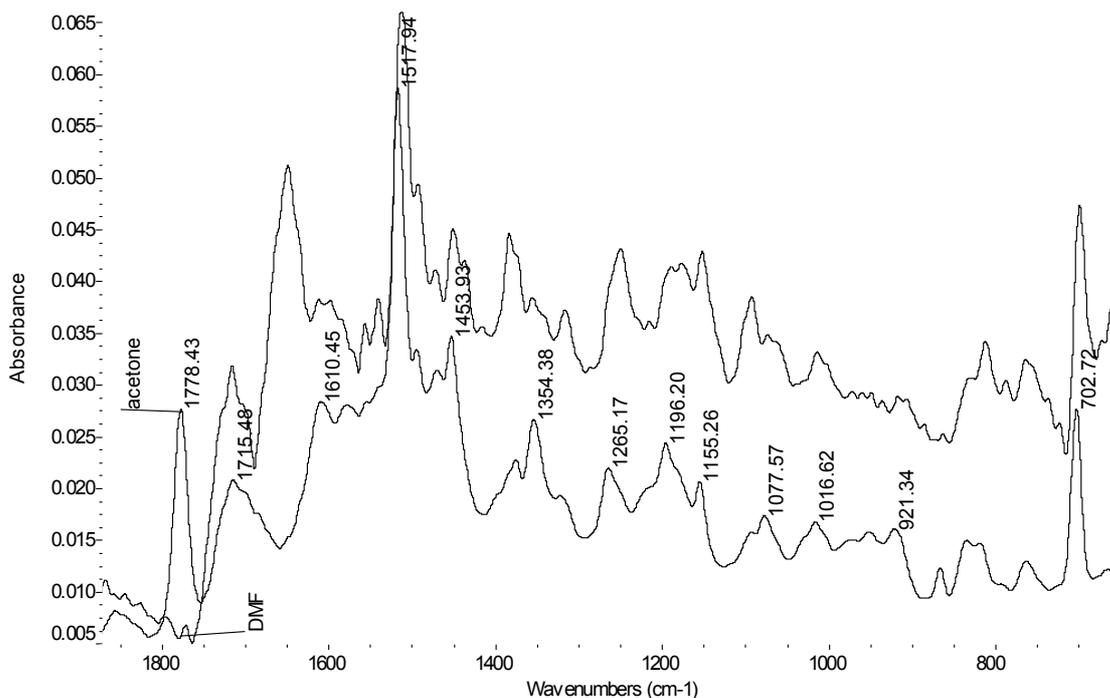


Fig. 6 – FTIR spectra of the reaction products of SMA with PADEA obtained in acetone and DMF at different concentrations.
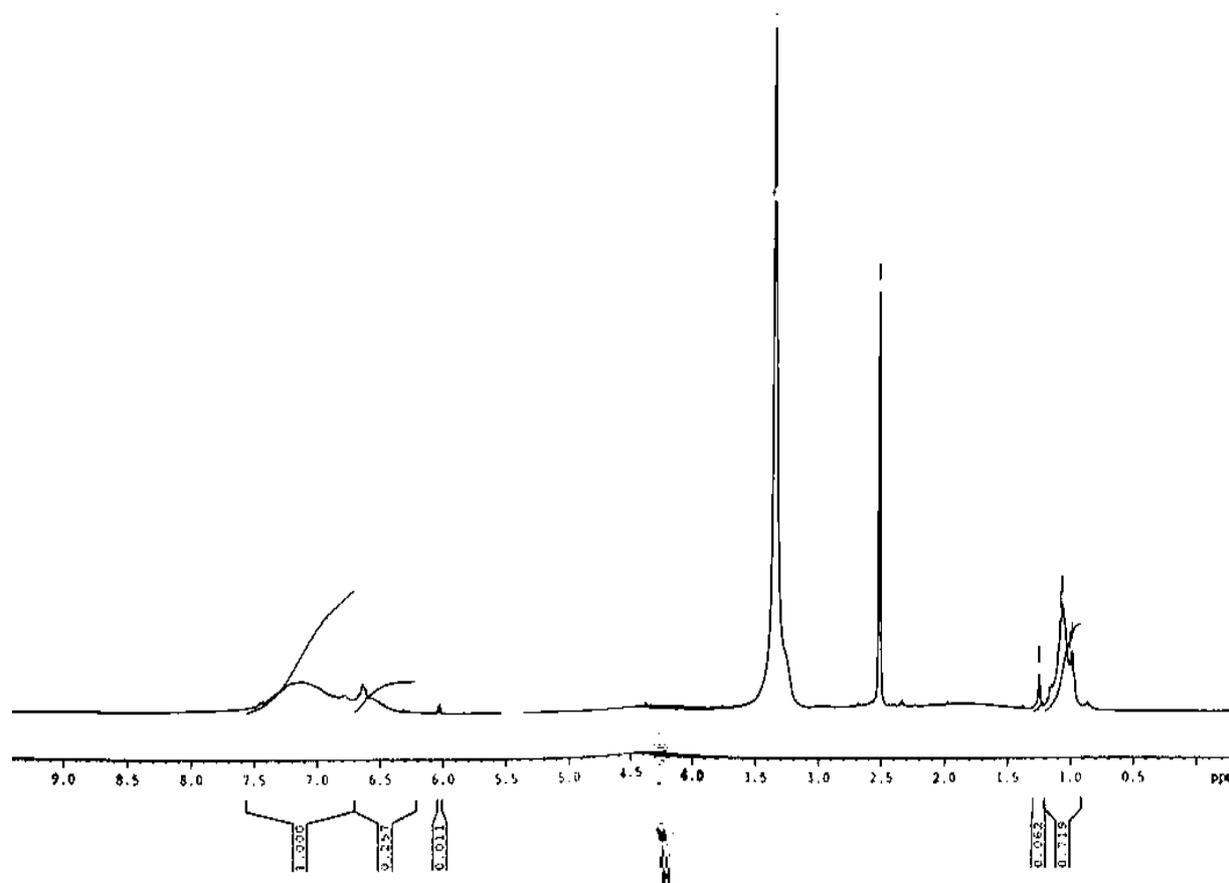
Fig. 7 – $^1$H-NMR (DMSO-$d_6$) spectrum of the reaction product of SMA with PADEA
(12 hours at room temperature, acetone as solvent).

In order to judge potential use of the transformed copolymer, we thought useful to investigate its thermal properties. In this respect we have carried out thermogravimetric and DSC measurements; the results are presented in Fig. 8. SMA copolymer (as such) shows a $T_g$ value around $189^0$C. We have found that the reaction product of SMA with PADEA exhibits a higher $T_g$ value (with around 19ºC) than the initial SMA; this behavior is in agreement with previously reported data on SMA after reaction with various amines.[25,26] Indeed, introduction of new bulky substituents increases the energy barrier for free rotation, and consequently the glass temperature.

The first section of TGA curve (10-300ºC) may be attributed to decarboxylation of the copolymer.[27] However, the most important weight loss (the "C" region between 300 and 500ºC) is probably due to degradation of side chain; it has to be said that such weight losses are smaller than those recorded for the untransformed copolymer (SMA). The destruction of the main chain begins at $500^0$C; the decomposition temperature is higher than that of SMA.[26,28]

## CONCLUSIONS

In this study, the chemical transformation of SMA with PADEA was described. The kinetic of the reaction between SMA and PADEA was investigated in acetone at room temperature. This reaction converts the anhydride group into the corresponding amide-acid, while the consecutive reaction of the generated acid with amine forming a diamide or imide was not noticed. Weight measurements have shown that amidation of SMA takes place faster in acetone at room temperature, than in DMF, upon heating. FTIR was instrumental in identifying amidation products; peaks corresponding to the amide function were better resolved for the product obtained in DMF. All UV spectra for the reaction products exhibit a peak at 282 nm, accompanied by a shoulder at 267 nm. NMR spectra added experimental proof for the proposed structures for the reaction product. The thermal properties of the transformed copolymer significantly differ (the value for $T_g$ is higher) from those of the initial SMA.
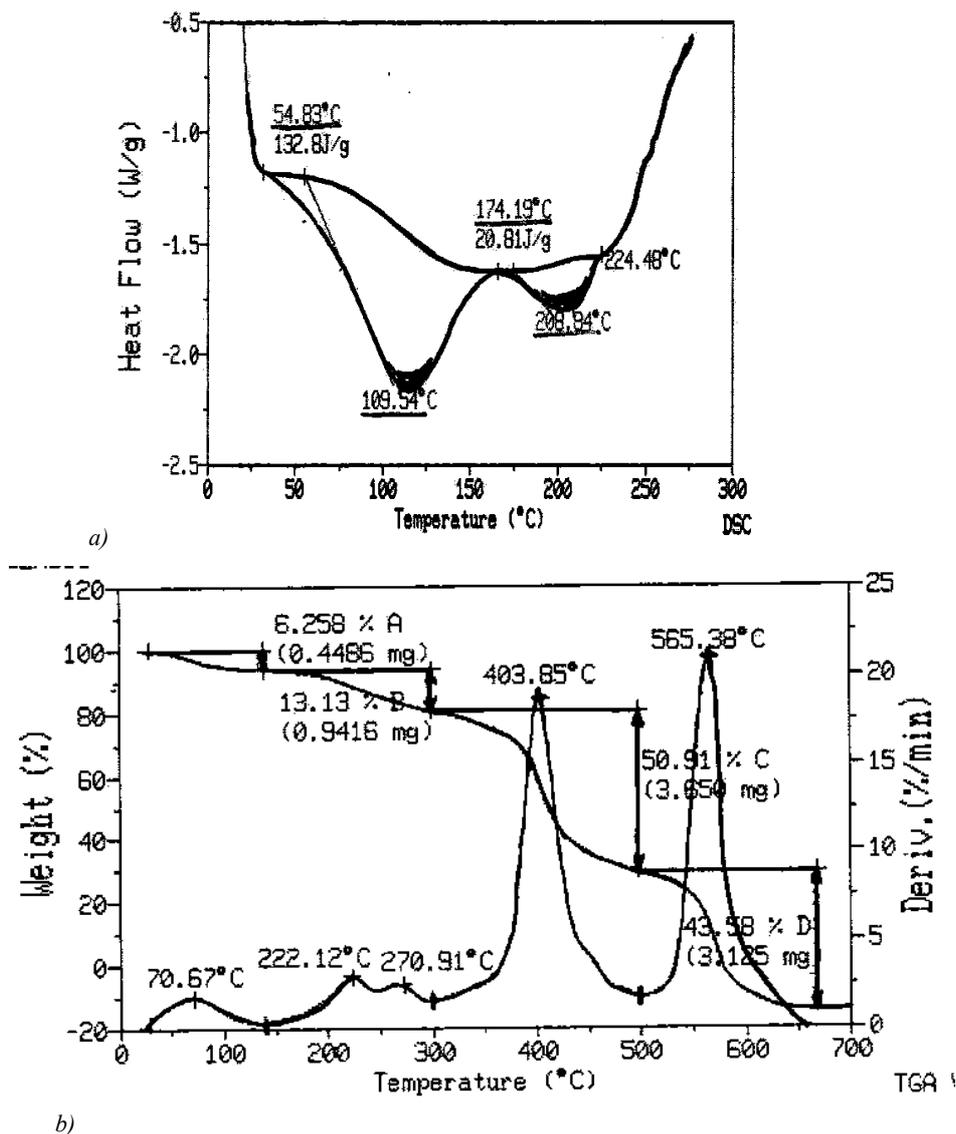
Fig. 8 – a) DSC graph for the reaction product of SMA with PADEA;
b) Thermogravimetry for the same product (heating rate 20º/minute).

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