STYRENE–DIVINYLBENZENE COPOLYMERS FUNCTIONALIZED WITH AMINOACID GROUPS: SYNTHESIS, PHYSICOCHEMICAL CHARACTERIZATION

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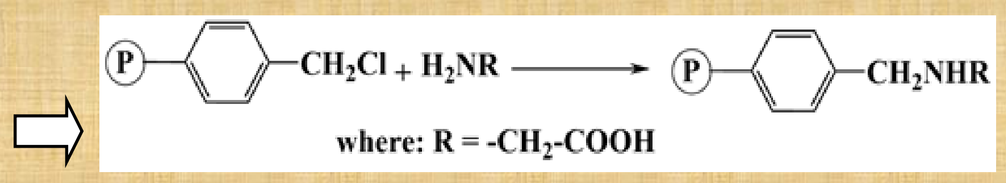
INTRODUCTION

- **Styrene-divinylbenzene (S-DVB) resins are synthetic copolymers known for their chemical resistance, mechanical durability, and good porosity. By adjusting the degree of crosslinking, their physical characteristics can be tailored for specific uses [1]. Amino acids contain functional groups such as amines (-NH_2), carboxylic acids (-COOH). Many of them are natural and non-toxic, making them ideal for applications in biomedical devices, drug delivery, and tissue engineering [2, 3].**
- **This work investigates the physicochemical characterization of two poly(styrene-co-divinylbenzene) copolymer supports, (containing 6.7% and 15% DVB), functionalized with glycine. The resulting copolymers were characterized using FTIR spectroscopy, TGA, EDX and SEM. The degree of amino acid functionalization was estimated by statistical modeling of the repeating structural units and through analysis of nitrogen content.**

EXPERIMENTAL

Chemical modification styrene-divinylbenzene copolymer

In a flask equipped with a thermometer, stirrer and refrigerant for reflux, 6 grams of the styrene-15%divinylbenzene copolymer (%Cl=11.93; G_F = 3.36 mmoles/g copolymer) (Code: S15DVBCH_2Cl) / styrene-6.7%divinylbenzene (%Cl = 14.22; G_F= 4.01 mmoles/g copolymer) (Code: S6.7DVBCH_2Cl) and glycine (NH_2CH_2COOH) were introduced at a molar ratio of 1:1 compared to the pendant group (–CH_2Cl). Glycine was previously dissolved in 100ml/75ml ethanol/distilled water solution. The synthesis took place for 30 hours at a temperature of 70°C. The final product was filtered, washed with hot distilled water and ethanol, and dried at 50 °C for 24 hours. The samples were noted AP1 and AP2 (see Scheme 1).

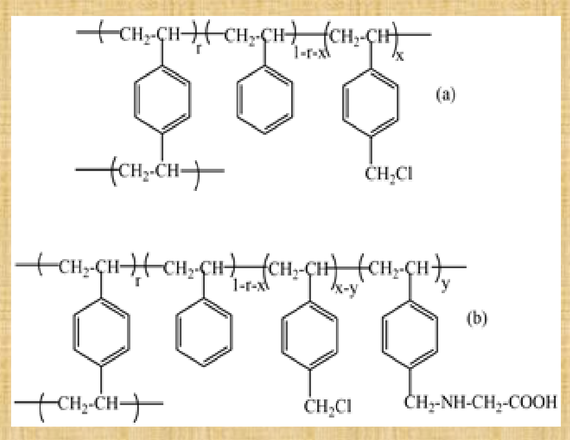


Scheme 1. The obtaining of the tested copolymers (AP1 and AP2).

RESULTS AND DISCUSSIONS

Table 1. EDX characteristics of the copolymers.

Elem.	Wt%	
	AP1	AP2
C	88.64	90.54
N	0.45	0.47
O	8.84	7.69
Cl	2.07	1.18



Scheme 2. Statistical structure of the repetitive unit of the (S15DVBCH_2Cl and S6.7DVBCH_2Cl) initial copolymer (a) and (AP1; AP2) final functionalized copolymer (b).

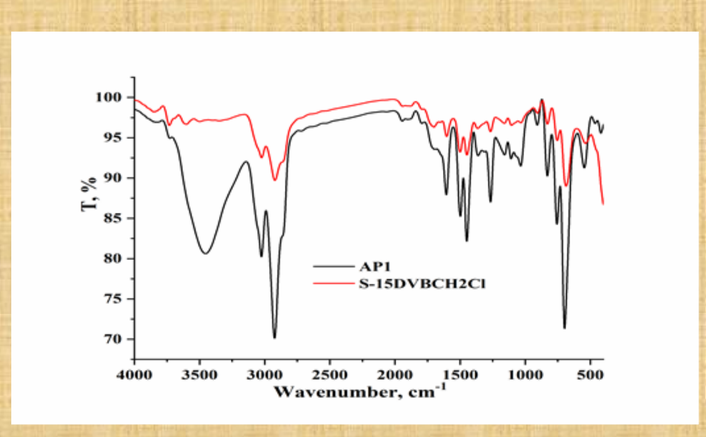


Figure 1. FTIR spectra for AP1 and initial support.

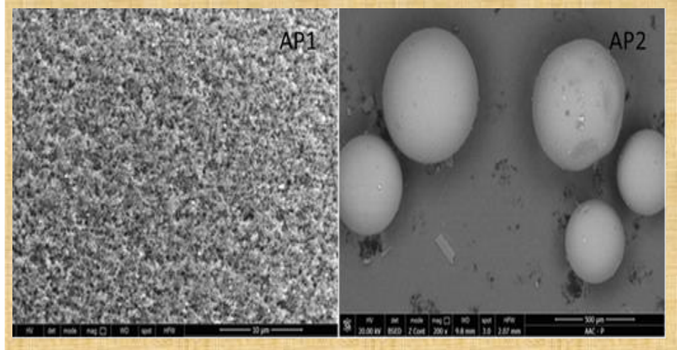


Figure 2. SEM image for AP1 and AP2

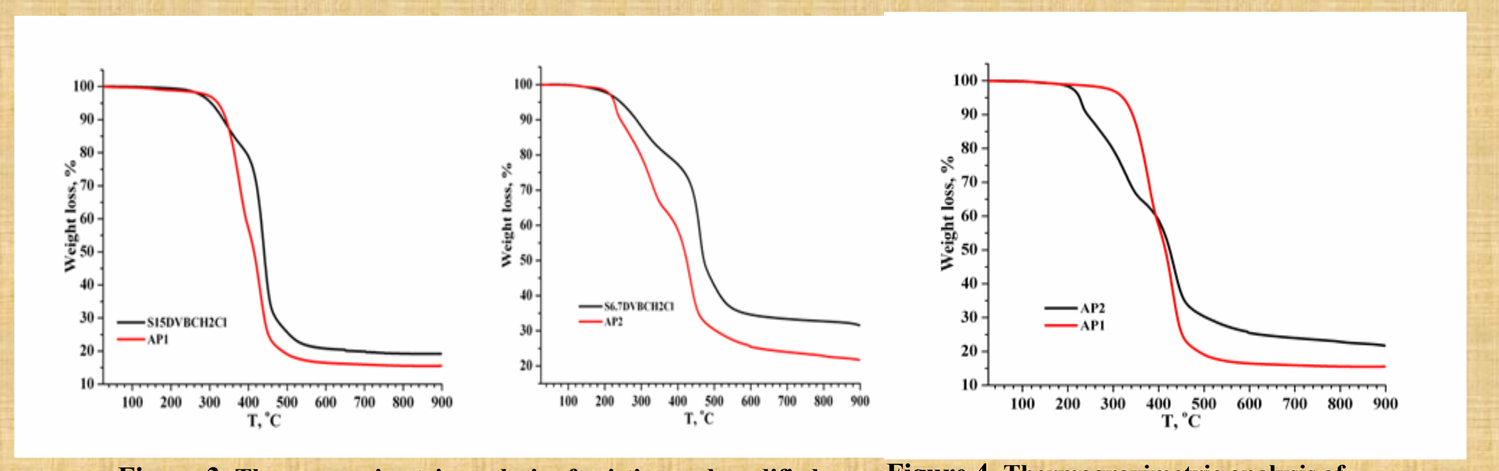


Figure 3. Thermogravimetric analysis of pristine and modified copolymers (AP1 and AP2), in nitrogen atmosphere.

Figure 4. Thermogravimetric analysis of modified copolymers (AP1 and AP2), in nitrogen atmosphere.

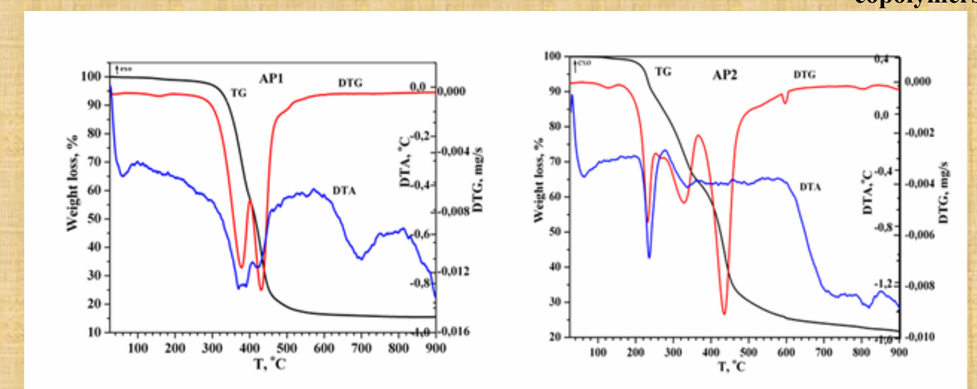


Figure 5. TG-DTG-DTA curves for AP1 and AP2 recorded in nitrogen atmosphere.

References:

1. Karabacak, M.; Kurt, M. *J. Mol. Struct.* 2009, 919, 215–222.
2. Arjunan, V.; Balamourougane, P.S.; Mythili, C.V.; Mohan, S. *J. Mol. Struct.* 2011, 1003, 92–102.
3. Boukaoud, A.; Chiba, Y.; Sebbar, D. *Vib. Spectrosc.* 2021, 116, 103280.

CONCLUSIONS

- **FTIR analysis shows shifts in C=O, C–N, and C–H bands at 1510–1365 cm^{-1} and broad OH/NH absorption at 3510 cm^{-1}, confirming the copolymer's successful functionalization with aminoacid groups. From the SEM image it can be seen that the surface of the microspheres remained clean and largely unchanged after the reaction to obtain AP1 and AP2.**
- **EDX analysis of AP1 and AP2 confirmed the presence of nitrogen, with concentrations ranging from 0.4% to 0.5%. Using statistical modeling of the repeating structural unit of the functionalized copolymers and the nitrogen content, the degree of functionalization with aminoacid type groups were for AP1: 0.321 mol/g; and AP2: 0.333 mol/g.**
- **Thermal stability, as indicated by residual mass at 900 °C, follows the trend:S-6.7%DVBCH_2Cl > AP2 (21.72%) > S-15%DVBCH_2Cl > AP1 (15.52%). This sequence highlights that AP2 is more thermally stable than AP1, likely due to structural differences such as the extent of crosslinking. AP1 exhibits a greater mass loss (84.48%) compared to S-15%DVB (80.82%), indicating a more significant degradation of its polymer structure. AP2 shows a slightly lower weight loss (78.28%), suggesting improved thermal stability, likely due to structural modifications involving amino acid functional groups. The raw material S-6.7DVB copolymer leaves a higher residue (31.58%) compared to AP2 (21.72%), suggesting that the raw material sample is more thermally resistant.**
- **The functionalization of amino acid groups onto styrene-divinylbenzene copolymers (AP1 and AP2) reduces the thermal stability of the copolymers, as evidenced by increased weight loss and lower char residues.**

Acknowledgements: This work was partially supported by Program 2 of Romanian Academy, "Coriolan Dragulescu" Institute of Chemistry