chemistry proceedings

MDPI

Proceeding Paper

Styrene–Divinylbenzene Copolymers Functionalized with Aminoacid Groups: Synthesis, Physicochemical Characterization †

Adriana Popa [1,*], Aurelia Visa [1], Laura Cocheci [2], Lavinia Lupa [2], Milica Țară-Lungă Mihali [1] and Ecaterina Stela Dragan [3]

[1] "Coriolan Drăgulescu" Institute of Chemistry, 24 Mihai Viteazul Blv., 300223 Timisoara, Romania; avisa@acad-icht.tm.edu.ro (A.V.); milicamihali22@gmail.com (M.Ț.-L.M.)
[2] Faculty of Chemical Engineering, Biotechnology and Environmental Protection, Politehnica University Timișoara, 6 Vasile Parvan Blvd., 300223 Timisoara, Romania; lavinia.lupa@upt.ro (L.C.); laura.cocheci@upt.ro (L.L.)
[3] "Petru Poni" Institute of Macromolecular Chemistry, 41A Aleea Grigore Ghica Vodă, 700487 Iași, Romania; sdragan@icmpp.ro
* Correspondence: apopa_ro@yahoo.com or apopa@acad-icht.tm.edu.ro
† Presented at the 29th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-29); Available online: https://sciforum.net/event/ecsoc-29.

Abstract

This work investigates the physicochemical characterization of two poly(styrene-co-divinylbenzene) copolymer supports, containing 6.7% and 15% divinylbenzene, functionalized with glycine. The resulting copolymers were characterized using Fourier Transform Infrared Spectroscopy, Thermogravimetric Analysis, Energy Dispersive X-ray Spectroscopy, and Scanning Electron Microscopy. The degree of amino acid functionalization was estimated by statistical modeling of the repeating structural units and through analysis of nitrogen content. Thermogravimetric Analysis(TGA) was further employed to investigate the impact of grafted amino acid groups on the thermal stability and decomposition behavior of the copolymers.

Keywords: aminoacid groups; styrene-divinylbenzene; functionalized copolymer

Academic Editor(s): Name

Published: date

Citation: Popa, A.; Visa, A.; Cocheci, L.; Lupa, L.; Dragan, E.S. Styrene–Divinylbenzene Copolymers Functionalized with Aminoacid Groups: Synthesis, Physicochemical Characterization. *Chem. Proc.* **2025**, *volume number*, x. https://doi.org/10.3390/xxxxx

1. Introduction

Styrene-divinylbenzene (S-DVB) resins are synthetic copolymers valued for their chemical stability, mechanical strength, and adjustable porosity [1]. They can be used in ion exchange, chromatography, and catalysis, these resins can be synthesized with varying degrees of crosslinking to tailor their physical properties. By adjusting the degree of crosslinking, their physical characteristics can be tailored for specific uses [2].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 [3].

In the present article, two poly(styrene-*co*-divinylbenzene) supports, having both 6.7% and 15% functionalized degree of divinylbenzene have reacted with glycine for obtaining aminoacid groups grafted on support. The synthetized copolymers were characterized by various techniques, namely Fourier transform infrared (FTIR), thermogravimetric analysis, the energy dispersive X-ray analysis (EDX) and scanning electron microscopy. Using

statistical modeling of the repeating structural unit of the functionalized copolymers and the nitrogen content, the degree of functionalization with aminoacid type groups was done. Thermogravimetric analysis was used to evaluate how specific functional groups, introduced via aminoacid grafting, influence the thermal decomposition behavior of the copolymers.

2. Experimental Part

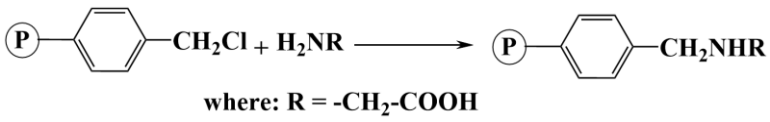
2.1. Materials and Methods

The chloromethylated copolymer styrene-15% divinylbenzene is raw materials received from the Institute of Macromolecular Chemistry "Petru Poni" Iasi and chloromethylated copolymer styrene-6.7% divinylbenzene supplied by Purolite Victoria Romania.

The thermal properties of the new polymeric products were characterized through thermogravimetric analysis on a TGA/SDTA 851-LF1100—Mettler machine (Switzerland) at a heating rate of 10 °C/min and temperature range from 25 to 900 °C. The experiments were carried out in nitrogen atmosphere at a flow rate of 50 mL·min^{-1}. The energy dispersive X-ray analysis (EDX) and study the surface morphology of the functionalized copolymers were performed using a Quanta FEG 250 microscope—at an accelerating voltage of 20 kV—(FEI Company, Nederland).

2.2. Obtaining of Aminoacid Groups Grafted onto Styrene-Divinylbenzene Copolymer

The syntheses for obtaining AP1 and AP2 (Scheme 1) were carried out according to method that we have previously published [4]. In a flask equipped with a thermometer, stirrer and refrigerant for reflux, 6 g of the styrene-15%divinylbenzenecopolymer (%Cl = 11.93; G_F = 3.36 mmoles/g copolymer) (Code: S15DVBCH$_2$Cl) / styrene-6.7%divinylbenzene (%Cl = 14.22; G_F = 4.01 mmoles/g copolymer) (Code: S6.7DVBCH$_2$Cl) 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 100 mL/75 mL ethanol/distilled water solution. The synthesis took place for 30 h 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 h. The samples were noted AP1 and AP2.



Scheme 1. Obtaining of AP1 and AP2 samples.

3. Results and Discussion

3.1. Characterization of Aminoacide Functionalized onto Styrene-Divinylbenzene Copolymers

The two samples AP1 and AP2 were characterized by EDX and SEM analysis.

The EDX spectrum in Figure 1 and the data in Table 1 confirm the reaction between the styrene-divinylbenzene copolymers and the aminoacid.

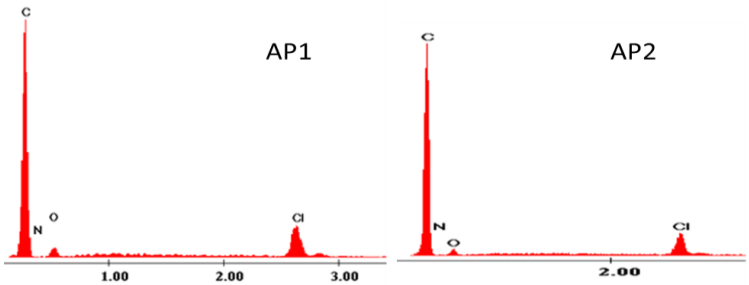


Figure 1. EDX image for AP1 and AP2.

Table 1. Semi-quantitative EDX-analysis of AP1 and AP2.

Element/ Sample	Wt %			
	C	N	O	Cl
AP1	88.64	0.45	8.84	2.07
AP2	90.54	0.47	7.69	1.18

Figure 2 shows that the surface of the microspheres remained clean and largely unchanged after the reaction to obtain AP1 and AP2.

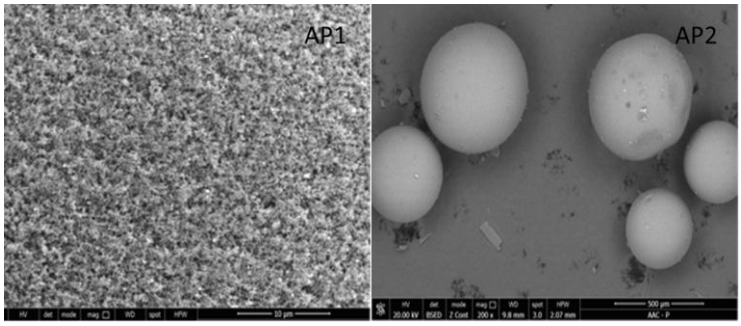


Figure 2. SEM image for AP1 and AP2.

Figure 3 shows the FTIR spectra of the starting copolymer and compound AP1. The FTIR spectrum of AP1 shows a slight shift of the C=O stretching band observed at 1615 cm^{-1}, suggesting a change following functionalization [5]. It is important to note that in this region (1700–1600 cm^{-1}) the interpretation is slightly hampered due to the overlap with the vibrations of the water molecule. Water, even in residual amounts, exhibits a H–O–H bending vibration around 1640 cm^{-1}, which overlaps with the carbonyl band, potentially masking or distorting the real differences between the precursor and API. In addition, the broad band observed at 3510 cm^{-1} is attributed to the O–H and N–H stretching vibrations, but may also be partially influenced by adsorbed moisture. Also, the general similarity between the FTIR spectra of the precursor and AP1 can be explained by the fact that the basic structure of the copolymer is preserved, and the chemical modification (introduction of an amino acid group) does not significantly affect the other major functional groups. However, an intensification of the band in the region 1510–1365 cm^{-1}, attributed to the C–N, C–H, and C=O vibrations of the amino acid moieties [6,7], indicates the presence of the new functionalization.

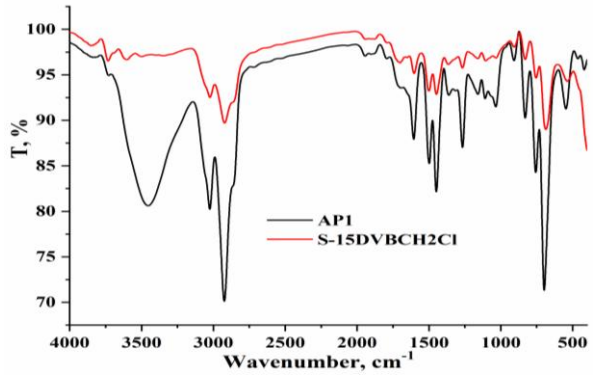
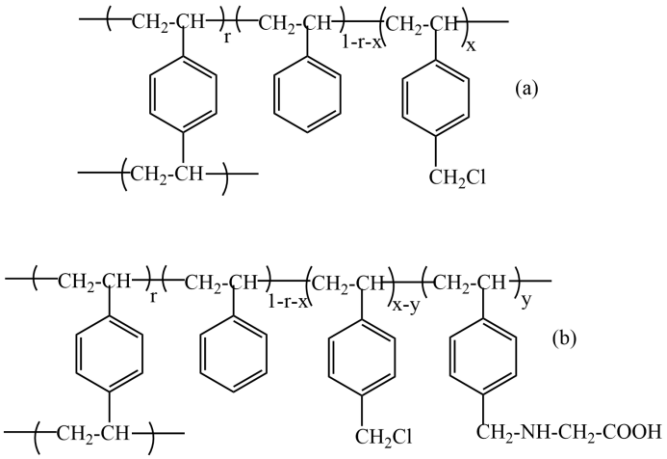


Figure 3. FTIR spectra for AP1 and initial support.

Using statistical modeling of the repeating structural unit of the functionalized copolymers and the nitrogen content, the degree of functionalization with aminoacid type groups was done. Scheme 2, shows the statistical structure of the repeating unit of the copolymers (AP1 and AP2) with functional groups of the amino acid type.



Scheme 2. Statistical structure of the repetitive unit of the (S15DVBCH$_2$Cl and S6.7DVBCH$_2$Cl) initial copolymer (**a**) and (AP1; AP2) final functionalized copolymer (**b**).

The notations used in Scheme 2 and Table 2 are as follows: F_f, aminoacid groups; F_i, CH_2Cl groups; x, fraction of styrene units bearing pendant-CH_2Cl initial groups; r, fraction of divinylbenzene (DVB) units; y, fraction of styrene units bearing pendant-aminoacid groups (Ff); %N, nitrogen percentage in the final copolymer; A_N, atomic weight of nitrogen; n_N, number of nitrogen atoms in the pendant groups; M_{mi}, average molecular weight of the repetitive unit of the initial copolymer; M_{mf}, average molecular weight of the repetitive unit of the final copolymer; M_S, molecular weight of the repetitive unit of styrene; M_{DVB}, molecular weight of the repetitive unit of divinylbenzene; M_{SFi}, molecular weight of the repetitive unit of the styrene functionalized with F_i (CH_2Cl) groups; M_{SFf}, molecular weight of the repetitive unit of the styrene functionalized with F_f (aminoacid) groups; G_F, functionalization degree.

Table 2. The characteristics of aminoacid groups functionalized onto copolymers.

Code	N (%,Wt)	x	Y [a]	M_{mi} [b]	M_{mf} [c]	G_F aminoacid (mmol/g) [d]
AP1	0.45	0.36	0.035	107.12	108.46	0.321
AP2	0.47	0.51	0.043	127.32	128.97	0.333

where: [a] $y = \frac{\%N \times Mmi}{100 \times n \times A_N - \%N \times (M_{SFf} - M_{SFi})}$; [b] $M_{mi} = r \times M_{DVB} + x \times M_{SFCH2Cl} + (1-r-x) \times M_S$; [c] $M_{mf} = M_{mi} + y(M_{SFf} - M_{SFi})$; [d] $G_F = \frac{y}{M_{mf}}$.

3.2. Thermal Stability of Aminoacide Functionalized onto Styrene-Divinylbenzene Copolymers

The TGA data for the pure and amino acid modified copolymers reveal notable differences in thermal stability and decomposition behavior (see Figures 4 and 5). The TG (thermogravimetric) analysis (see Figures 4 and 5) for the pure copolymers S-15DVBCH2Cl and AP1 clearly indicate differences in thermal stability and decomposition behavior, based on residue and weight loss data at 900 °C:—S-15%DVB exhibits higher thermal stability than AP1, as indicated by a higher residue (19.18% vs. 15.52%). This

suggests that the incorporation of the aminoacid group in the AP1 sample leads to a more complete thermal decomposition. AP1 loses more mass (84.48%) than S-15%DVB (80.82%), supporting the idea that the AP1 structure degrades more significantly or contains components with less thermal stability. Analyzing the TG (sees Figure 4 and 5) for the copolymers S-6.7DVBCH2Cl and AP2 clearly indicates differences in thermal stability and decomposition behavior, based on residue and weight loss data at 900 °C: —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 higher weight loss (78.28%) in AP2 indicates a higher degradation, possibly due to changes in the polymer structure with amino acid groups. The differences in total weight loss and final residues suggest that the AP2 copolymer may decompose more completely.

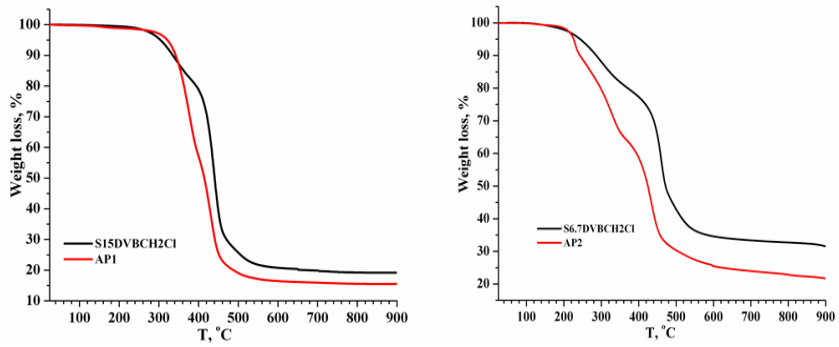


Figure 4. Thermogravimetric analysis of pristine and modified copolymers (AP1 and AP2), in nitrogen atmosphere.

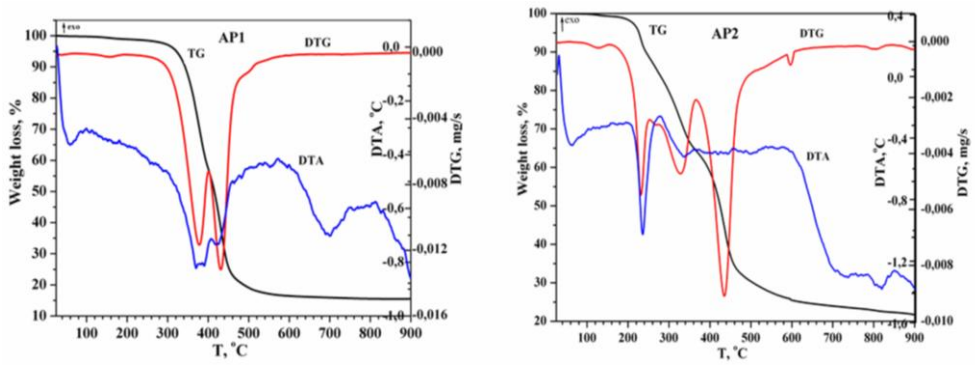


Figure 5. TG-DTG-DTA curves for AP1 and AP2 recorded in nitrogen atmosphere.

Thermogravimetric analysis (see Figure 5) was used to evaluate the thermal behavior of two styrene-divinylbenzene copolymers functionalized with aminoacid, denoted AP1 and AP2. From the weight loss percentages, information can be obtained about the structural stability of the polymer backbone. The TGA curves for both AP1 and AP2 showed three main weight loss stages. The initial weight loss observed below 150 °C was attributed to the loss of adsorbed moisture, which is amplified by the hydrophilic nature of the amino and carboxyl groups of glycine. The second and most significant decomposition stage occurred between approximately 150 °C and 400 °C, corresponding to the thermal degradation of the glycine functionalities. The third stage, which occurs above 400 °C, was associated with the decomposition of the S-DVB polymer backbone. The total mass losses recorded were 84.48% for AP1 and 78.28% for AP2, indicating substantial thermal decomposition.

The thermal stability, for all analyzed samples, indicated by the residual mass at 900 °C, follows the following sequence: S-6.7%DVBCH$_2$Cl > AP2 (21.72%) > S-

15%DVBCH$_2$Cl > AP1 (15.52%). This sequence highlights that AP2 is more thermally stable than AP1, probably due to structural differences, such as the degree of crosslinking (see Figure 6). Divinylbenzene (DVB) also plays a key role in the crosslink density.

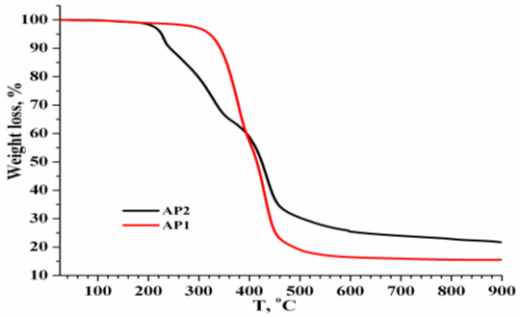


Figure 6. Thermal stability comparison (between AP1 and AP2), in nitrogen atmosphere.

4. Conclusions

The functionalization of aminoacid 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. These modifications likely introduce thermally fewer stable moieties and alter the decomposition pathways. Thermal stability (based on residue) follows: S-6.7DVBCH2Cl > AP2 (copolymer residue = 21.72%) > S-15%DVBCH2Cl > AP1 (copolymer residue = 15.52%). This suggests AP2 is more thermally stable than AP1. The pristine copolymers exhibit significantly higher thermal resistance, suggesting that both AP1 and AP2 have a more degradable structure due to functionalization. The aminoacid content confirms the potential applicability of these materials in metal ion chelation, ion exchange, or bioconjugation applications.

Author Contributions: Conceptualization, A.P. and L.C.; methodology, A.P., L.C. and A.V.; formal analysis, L.C., L.L. and E.S.D.; investigation A.P., L.C. and A.V.; data curation, A.P., L.C., L.L. and A.V.; validation, L.C., A.P. and E.S.D.; writing—review and editing, A.P., M.Ț.-L.M. and L.C.; manuscript revisions, A.P., L.L. and E.S.D.; supervision, A.P. and L.C.; project administration, A.P. and L.C. All authors have read and agreed to the published version of the manuscript.

Funding:

Institutional Review Board Statement: Not applicable.

Informed Consent Statement:

Data Availability Statement: The original contributions presented in this study are included in the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Teixeira, V.G.; Coutinho, F.M.B.Morphological study on the reactivity of styrene-divinylbenzene copolymers in a chloromethylation reaction. *J. Appl. Polym. Sci.***2010**, *118*, 2389–2396.
2. Ramos, G.S.M.; Mendes, M.S.L.; Neves, M.A.F.S.; Pedrosa, M.S.; da Silva, M.R. Experimental design to evaluate the efficiency of maghemite nanoparticles incorporation in styrene-divinylbenzene copolymers. *J. Appl. Polym. Sci.* **2021**, *138*, 50318.
3. Khan, W.S.; Muthupandian, S.; Farah, N.; Kumar, A.J. Domb, Biodegradable Polymers Derived From Amino Acids Macromol. *Biomaterials* **2011**, *11*, 1625–1636.
4. Cocheci, L.; Visa, A.; Maranescu, B.; Lupa, L.; Pop, A.; Dragan,E.S.; Popa, A. Glycine-group-functionalized polymeric materials impregnated with Zn(II) used in the photocatalytic degradation of congo red dye. *Polymers* **2025**, *17*, 641.

5. Karabacak, M.; Kurt, M. The spectroscopic (FT-IR and FT-Raman) and theoretical studies of 5-bromo-salicylic acid. *J. Mol. Struct.* **2009**, *919*, 215–222.
6. Arjunan, V.; Balamourougane, P.S.; Mythili, C.V.; Mohan, S. Experimental spectroscopic (FTIR, FT-Raman, FT-NMR, UV–Visible) and DFT studies of 2-amino-5-chlorobenzoxazole. *J. Mol. Struct.* **2011**, *1003*, 92–102.
7. Boukaoud, A.; Chiba, Y.; Sebbar, D. A periodic DFT study of IR spectra of amino acids: An approach toward a better understanding of the N-H and O-H stretching regions. *Vib. Spectrosc.* **2021**, *116*, 103280.