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Poly(butadiene-acrylic acid(g)acrylonitrile(g)acrylic acid)

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SUMMARY

In the present work we describe the synthesis and characterization of a new gel obtained by crosslinking a cooligomer of butadiene-acrylic acid (BuAA),by reaction with acrylonitrile and acrylic acid. The purified product was characterized by FTIR, elemental analyses and scanning electronic microscopy.The thermal properties were studied and swelling indexes were determined in different solvents and at different pH values.The capacity of poly(butadiene-acrylic acid(g)acrylonitrile(g)acrylic acid) [gel A] to separate different organic substances, such as amino acids and colorants, was determined.

INTRODUCTION

The separation and purification of organic compounds, especially biological molecules, is still a difficult problem and in many instances this requires techniques with high resolution.The use of chromatography is one of the best alternatives. The synthesis of new resins able to be used as matrices with specific properties is an important area in polymer science.(1)

In the present work we have investigated the preparation and characterization of a new gel from BuAA crosslinked with acrylonitrile and acrylic acid and studied its possible application as support in ionic interchange.

The incorporation to a macromolecule with a polybutadiene chain (hydrophobic) of carboxylate and nitrile groups yielded a new resin, with good thermal properties, able to swell both in organic solvents or in aqueous solutions and showing specific ability to retain different cationic substances.

EXPERIMENTAL

SYNTHESIS

This product was synthesized using a purified fractionated cooligomer BuAA by crosslinking with acrylic acid and acrylonitrile .The cooligomer BuAA (Mw = 5000 by VPO) was synthesized by bulk polymerization using 1,3-butadiene and acrylic acid and benzoyl peroxide as initiator(2);it was purified by fractional precipitation using benzene as solvent and methanol as non-solvent.Fractions F_1, F_2 and F_3 were collected.

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The gel A was obtained from F_1, which reacted with acrylic acid and acrylonitrile in a ratio 1:1:1 w,w,w respectively.The reaction was carried out in a 250 ml flask equipped with a mechanical stirrer and condenser.In a typical graft polymerization, BuAA was dissolved in dry benzene.The reaction mixture was purged with nitrogen for 15 minutes adding afterwards acrylic acid, acrylonitrile and initiator (1% benzoyl peroxide).The reaction was carried out at 80 °C , for two and a half hours.

An insoluble swellable gel was obtained. It was purified by several washes in a column with benzene, until no more soluble products were eluted and was finally dried in a vacuum system.

Swelling indexes were determined by the ratio V_i(volume of swelled gel) and V_0(volume of dry gel), $I=V_i/V_0$.

The gel characterization was carried out by IR spectroscopy, and differential scanning calorimetry (DSC) determined on a Nicolet 5-sxc spectrophotometer, Fourier transform infrared (FTIR) and a Beckman Instrument (INTEC),respectively.

Thermogravimetric determinations and scanning electron microscopy were made in the Research Centre of Materials and Metrology, following conventional techniques.Elemental analyses were carried out by UMYMFOR.

COLUMN EXPERIMENTS

The applicability of this gel for the retention of organic substances was studied using a glass column. Gel A was used to retain different substances such as cationic dyes and amino acids.The dried gel was mixed with a solution of NaOH 0.1 N; obtaining the sodium salt after maintaining at pH 12 for 48 hours. The gel was washed abundantly with distilled water until neutral, and the swelled gel was packed into a 20 x 1 cm glass chromatographic column .The gel in the column was extensively washed before use.The samples were applied to the top of the column in 0.5 ml buffer solutions and elution was carried out with the same buffer solution. Fractions of 1 ml were taken.

The maximum capacity of the resin for sodium was determined using 0.100 gr of the dry gel A with a solution of NaOH, 0.1 N.

In order to measure amino acid retention, a colorimetric technique was used , with ninhidrine(3) observing saturation of the column. Then the amino acids were desorbed using a solution of NaOH and determined in a SHIMADZU UV-visible Spectrophotometer after reaction with a solution of ninhidrine (4).The other substance used was, malachite green. The retention of this dye was determined by visible spectroscopy (malachite green λ_{max}=619.9nm)

RESULTS AND DISCUSSION

SYNTHESIS and CHARACTERIZATION

Determinations of the swelling indexes of the gel, in different solvents and at different pH are summarized in Tables 1 and 2, respectively. It can be observed that the purified gel obtained swelled well in DMF , MeOH and buffer solution at pH 9.

TABLE 1: Swelling indexes in organic solvents

solvent	**n-hexane**	**benzene**	**toluene**	**chloroform**	**MeOH**	**DMF**
swelling index	1	1.5	1.6	3	3.5	5

TABLE 2: Swellig indexes in buffer solutions at different pH

pH	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
swelling Index	**1.5**	**1.5**	**1.5**	**1.8**	**3.5**	**5.5**	**6**	**6.5**	**7**	**6.5**	**6.3**	**6**	**5**

The IR spectra of the purified gel showed a new signal compared with oligomer BuAA.Absorption at 2242 cm-^{1} was attributed to the cyano groups incorporated into the structure.Other new bands can be observed at 750 cm^{-1} (-C=C-) , 911 cm-1 (C=CH2), 968 cm^{-1} (-C=C-), 1070-1170 cm^{-1}(-CH2), 1645 cm^{-1}(-C=C-), 1690 cm^{-1} (-C=O), and at 2850-3100 cm^{-1} (=CH and-CH).The DSC determination for the gel showed an endothermic peak at 37.1 °C. This temperature was considered as glass-transition.

Figure 1 shows that gel A is more stable than oligomer BuAA . The pendent cyano groups cyclize to thermally more stable aromatic structures as reported in the literature(5).

FIGURE 1: Thermogravimetric analyses

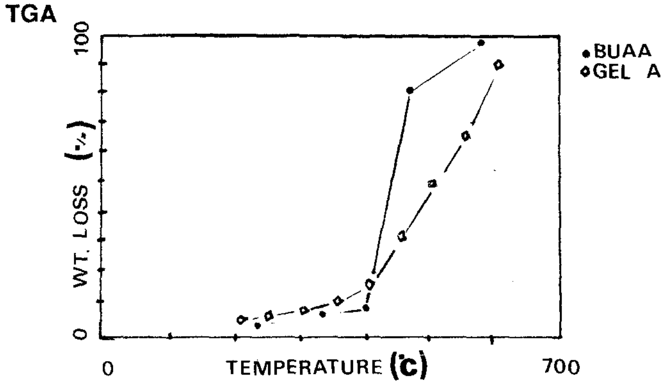
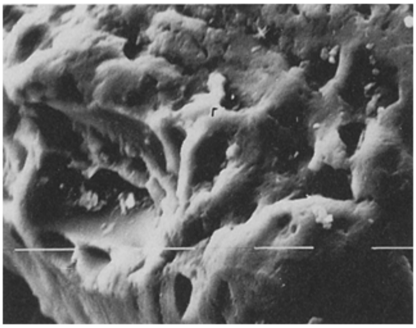


Figure 2 shows the surface of a new gel revealing porous characteristics.

FIGURE 2:SEM OF GEL A



The values obtained by elemental analyses of gel A were carbon: 70,28%, hydrogen: 6,19%, nitrogen: 9,22% and for oxygen: 14,31%

RETENTION FOR DIFFERENT SUBSTANCES

The maximum capacity of the gel for sodium was 5.11 meq/gr(of dry gel).The gel contains carboxylic groups which are able to retain sodium with a small volume easy to permeate through the porous surface of the hydrogel.

Other cations such as malachite green with a large molecular volume was retained in a 2.5 meq/gr concentration (of dry gel).

Results obtained in experiments with amino acids are given in Table 3.

TABLE 3:

aminoacids	**pH of the medium**	**meq/gr**
triptophane	7	none
threonine	7	none
lisine	7	0.126
arginine	7	0.8

The support showed a different capacity in the retention of different substances in agreement with pendent carboxylic groups.

Amino acids such as lisine and arginine with residual positive charges at the working pH were retained. In contrast, triptophane and threonine were not retained because at the working pH they lacked residual positive charges however, elution times from the column were different. It was evident that the retention obtained with this new gel was principally due to ionic interchange and also to coulombic interactions.

CONCLUSION

A new product was synthesized, which was characterized as a crosslinked structure swelling in different organic solvents and also in aqueous solutions to different extents according to the pH.

This new product showed a halflife temperature of 500 °C.

The gel is able to retain different cations, such as dyes and amino acids, by coulombic interactions.

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