Polymer Bulletin 22, 21–24 (1989)

Polymer Bulletin

Synthesis of diacetylenic-butadiene-acrylic acid block copolymers

M. Strumia, H. Bertorello, and G. Lescano

Departamento Química Orgánica, Facultad de Ciencias Químicas,
Universidad Nacional de Córdoba, 5016 Cordoba, Argentina

SYNOPSIS

This paper describes the synthesis and post-polymerization in solution of a copolymer 1,3-butadiene-acrylic acid modified with diacetylenic pendant groups. The products were characterized by UV, IR and NMR spectroscopy.

INTRODUCTION

Novel structures often provide opportunities for new applications. Diacetylenic polymers are excellent for these type of studies.

Several publications[1,2,3] inform us about the polymerization of diacetylenes. In most cases, this polymerization occurs in the solid-state to transform an array of monomer molecular into a polymer chain whose backbone is best represented by the structure $-(R)-C{\equiv}C-C{\equiv}C-(R)-$ (I), where R is a substituent group. However, very few examples about the solution properties of diacetylenic polymers have been reported in the literature, probable due to their low solubility.[4,5,6]

The work presented herein concerns the incorporation of a diacetylenic monomeric structure (I) into a butadiene-acrylic acid co-oligomer previously obtained by us.(I) was incorporated as pendant group along the polymer backbone. Polymerization of this modified oligomer led to soluble polymers showing different colors. Purification of the products together with solution and film studies were performed and are the subject of the present work.

EXPERIMENTAL SECTION

The resins containing diacetylenic groups were synthesized by using butadiene-acrylic acid co-oligomers as the starting material (Polymer 1). They were synthesized by bulk polymerization using 1,3-butadiene, acrylic acid and benzoyl peroxide as catalyst.[7] They were purified by fractional precipitation using benzene solvent and ethanol non-solvent. Fractions F_1, F_2 and F_3 were collected. The modified polymers were synthesized from F_1, F_2 and F_3.

In order to introduce the diacetylenic groups into polymer 1, the carboxyl groups were converted to chlorides using thionyl chloride (Fluka) in benzene at 0°C. In this way, polymer 2 was reacted with 10,12-docosadiyne-1,22-diol with a relation of 1 eq. -COOH:1.25eq. of I giving the polymer 3, 4 and 5. This reaction was performed at reflux in THF for

18 hours (See Scheme N° 1).

The polymeric products were purified by fractional precipitation and preparative G.P.C.

Determination of the carboxyl groups was carried out by titration using sodium hydroxide in methanol and thymol blue indicator. Measurements were made before and after esterification leading to approximate conversion percentages.

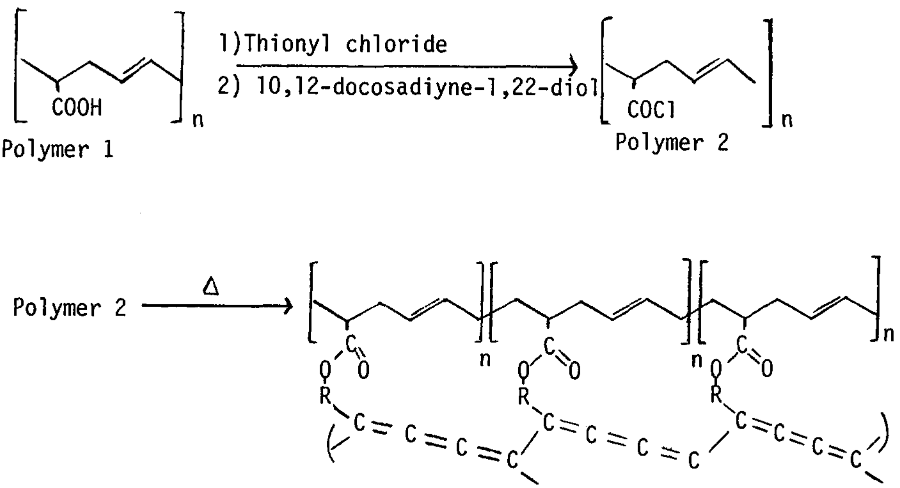
IR, UV and ^{1}H-NMR spectroscopy were obtained on a Nicolet 5-SXC spectrophotometer, FT-IR spectrometer, a Shimadzu UV-260 spectrophotometer and a Varian T-60 spectrophotometer, respectively. THF was used for UV spectroscopy studies and carbon tetrachloride for ^{1}H-NMR determinations.

RESULTS AND DISCUSSION

Synthesis

Polymer 3 obtained from fraction F_1 of the butadiene-acrylic acid co-oligomer (Polymer 1) with 0.16 eq.^{1}-COOH/100 gr. was an orange product insoluble in common organic solvents, such as CCl_4, THF, benzene, $CHCl_3$, etc. Nevertheless, this product was swellable in THF, benzene and $CHCl_3$ to orange gels.

Figure N° 1 Scheme of Synthesis.



Polymer 1

Polymer 2

Polymer 3, 4 and 5

The percent esterification of 1 to 3 was approximately 75%.

Polymer 4, a yellow product, was obtained from fraction F_2 of polymer 1 with 0.22 eq. -COOH/100gr. It was soluble in THF, benzene, $CHCl_3$ and CCl_4. The percent conversion of 1 to 4 was approximately 70%.

Polymer 5 was obtained from fraction F_3 of the polymer 1 with 0.54 eq. -COOH/100 gr showing initially a dark yellow color, but after purification by G.P.C. the raw product gave a blue, a green and yellow product. The percent esterification of 1 to 5 approximately 72%.

The different colors of polymers 3, 4 and 5 are evidence of the different extents of conjugation. Color changes vary with different conjugation length, short conjugated segments absorb in the blue region (yellow solutions) while long segments absorb in the red region (blue solutions).

Polymer 5 showed color changes with solvent change, the blue solutions in benzene were transformed into yellow solutions in CCl_4.

Following Schott and coworkers[4] who consider the probability for intramolecular conjugation, we suggest that in our case also mainly intramolecular polymerization occur. This is in accord with the fact that a long conjugation was obtained (green and blue solutions) from oligomers with a large amount or functionality. (e.g., F_3 with 0.54 eq. -COOH/100gr).

I.R. spectroscopy

The I.R. spectra exhibited bands at 715, 880 and 970 cm^{-1}, the out of plane deformations were assigned to the C-H bond for the 1,4 cis, vinyl and 1,4 trans units, respectively.

The other peaks were assigned to the following bonds: -OH: 3408 cm^{-1}; -C-H: 2900 cm^{-1}; $>C=O$: 1707 cm^{-1}; $>C=C<$: 1645 cm^{-1} -C=C=C- (doublet): 1958 and 1990 and $-C\equiv C-C\equiv C-$: 2211 cm^{-1} (very slow).

U.V. spectroscopy

In Table 1 are presented U.V. absorptions of the different polymers obtained. They show a strong band at aproximately 250 nm, corresponding to the $>C=O$ group and a weak band in the visible region attributable to conjugated structures between single, double and triple bonds.

Table 1: UV absorptions.

Product	$>C=O$	$(-C=C=C=C-)_n$
blue solutions	256	640
green solutions	-	654
yellow solutions	262	495
Polymer 1	229	-

^{1}H-NMR spectroscopy

The main assignment of the signals are: $=CH_2$(1,2 ad.): 1,45-2.00 ppm; $-CH_2$ (1,4 ad.) and =CH-(1,2 ad[2]): 2.00-2,50 ppm; -CH : 3.30-3.50 ppm; $-C\underline{H}=C\underline{H}-$ (1,4 ad.): 5.45; $-C\underline{H}=CH_2$ (1,2 ad.) 5.20 and $-CH=C\underline{H}_2$ (1,2 ad.): 4.95-5.50 ppm.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge CONICET and CONICOR for financial assitance. M. Strumia acknowledges receipt of a fellwship granted by CONICET.

BIBLIOGRAPHY

1.- Khandelwal P. and Talwar S. J. Polym. Sci 21 (11), 3073 (1983).
2.- Wynne K. and Bryan G. Ind. Eng. Chem. Prod. Res. Dev. 21, 23-28 (1982)
3.- Schur J. and Singh A. Polymer Preprints 26 (2), 186. (1985).
4.- Schott M., Chance R. et al. Polymer Preprint 27, (1), 65. (1986)
5.- Wenz G., Muller M. and Wegner G. Macromol 17, 837 (1984).
6.- Patel G. and Walsh E. J. Polym.Sci.: Polym. Lett. Ed. 17 (4), (1979).
7.- Argüello R. Tesis Doctoral. Fac. de Cs. Químicas. Univ. Nac. de Córdoba. Argentina (1981).

Accepted May 5, 1989 K