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Synthesis of epoxidized poly(1,3-butadiene-co-acrylic acid) resins

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SUMMARY

A copolymer of 1,3-butadiene with pendant carboxyl groups 1 was conveniently transformed into the corresponding epoxidized copolymer 2, Synthesis of copolymer 2 was carried out by epoxidation of double bonds present in copolymer 1.

INTRODUCTION

In the last years there has been a steadily increasing interest in the search of better properties by modifying preformed polymers, i.e. synthesis of epoxidized natural rubber. This synthetic polymer presents some improved properties with respect to natural rubber, i.e. better adhesion to humid surfaces and improved oil and solvent resistance (1,2).

Our laboratory is primarily interested in the synthesis and/or chemical modifications of polymers with potential applications as reactive polymers or as synthetic rubbers.

The work presented herein involves the synthesis of reactive oligomers of polybutadiene with carboxyl and oxirane groups along the polymer backbone.

EXPERIMENTAL

Synthesis of 1,3-butadiene-acrylic acid copolymer 1:

This copolymer was obtained by bulk polymerization at 70°C using benzoyl peroxide initiator at 1% wt/wt (3).

The polymer obtained was a liquid (Mn:3700 by V.P.O.) with a carboxyl content of 0.45 eq./100g of polymer and a viscosity of 0.098 dl/g in benzene.

Purification by fractional precipitation:

35g copolymer 1 were dissolved in 44ml benzene, using 88ml methanol as nonsolvent. The sample was stored at 5°C for 24hs. The resulting precipitate (F1) was dried at reduced pressure at room temperature. Carboxyl content of F1 was 0.21 eq./100g.

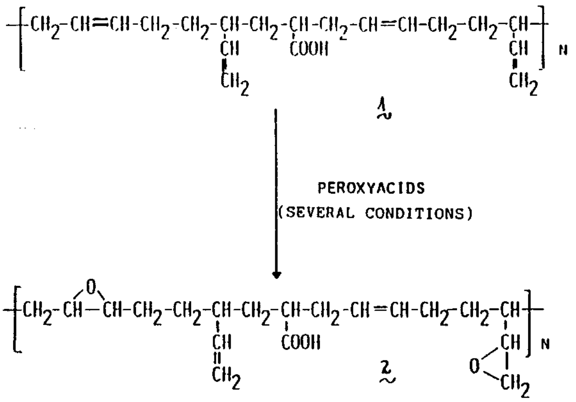

Figure 1
Scheme of synthesis of Copolymer 2.

A.- Epoxidation of copolymer 1 by peroxybenzoic acid:

Peroxybenzoic acid (0.21 moles) in 80ml chloroform was added slowly to 5.8g stirred copolymer 1 (F1) in 40ml benzene. After 4hs at room temperature, the reaction mixture was extracted with two portions (100ml) of saturated aqueous solution of sodium bicarbonate, two portions (100ml) of saturated aqueous solution of sodium chloride and two portions of distilled water. The organic solution was dried with anhydrous sodium sulfate and filtered; the solvents were evaporated (rotatory evaporator) and the epoxidized copolymer 2 was dried at reduced pressure. The oxirane group content was 0.26 eq./100g; it was determined by pyridinium chloride and hydrogen bromide methods (4,5).

B.- Epoxidation of copolymer 1 by peroxyacetic acid:

20ml peroxyacetic acid 0.9M (aqueous solution) were added slowly to 5.0g stirred copolymer 1 (F1) in 40ml benzene. After 4hs at room temperature, the reaction mixture was treated the same way as in A. Oxirane group content was 0.24eq./100g.

C.- Epoxidation of copolymer 1 by in situ generated peroxyacetic acid:

31ml hydrogen peroxide 50% wt/v were added dropwise to a mixture formed of 20.0g copolymer 1 (F1), 10ml glacial acetic acid, 2ml sulfuric acid 96% wt/wt, and 100ml benzene. The reaction mixture was heated at 50°C in a thermostated bath with magnetic stirring. During the reaction a white solid precipitated. This product was insoluble in: distilled water, methanol, benzene, o-dichlorobenzene, acetone, methylene chloride, ethanol and hexane. Oxirane group content was not determined due to the insolubility of the product.

D.- Epoxidation of copolymer 1 by in situ generated peroxyacetic acid using ion exchange resins:

I) Using anion exchange resin:

16ml hydrogen peroxide 50% wt/v were added slowly to a mixture of 2.10g copolymer 1 (F1), 15ml glacial acetic acid, 4.3g Amberlite IRA-458 (BDH), and 30ml benzene. The reaction was heated at 50°C in a thermostated bath with magnetic stirring for 2hs. The ion exchange resin was filtered and the resulting solution was treated in the same way as in A. Oxirane group content was 0.19 eq./100g.

II) Using cation exchange resin:

This reaction was carrried out under the same conditions as I. The reagents were: 3.1g copolymer 1 (F1), 6.3g Amberlite IRA-120 (BDH), 21ml glacial acetic acid, 23ml Hydrogen peroxide 50% wt/v, and 45ml benzene. Oxirane group content was 0.06 eq./100g.

Curing Process:

Samples of copolymers 1 and 2 were placed on KBr disks and heated at constant temperature (70°C) in a oven. At different times IR spectra were recorded by a Beckman IR 12 infrared spectrophotometer.

RESULTS AND DISCUSSION

The IR spectrum of copolymer 1 (Figure 2) showed the following resonance bands:

Signal (cm^{-1})	Group
1725	C=O
1450-1420	C=C
970	-HC=CH-(1,4 trans)
910	-HC=CH$_2$(1,2 vinyl)
690	-HC=CH-(1,4 cis)

The spectrum of copolymer 2 (Figure 3) showed similar absorption bands except for a relative increase in the band at 910cm^{-1}. This band is attributed to out of the plane vibration of the C-H bond due to 1,2 vinylic addition in copolymer 1, while in the copolymer 2, the additional contribution is due to the presence of oxirane groups which are also absorved at the same frequency.

Table 1 shows the ratios of the absorbances at 910cm^{-1} in copolymers 1 and 2 with respect to the carboxyl band arising from the acrylic acid which remains unchanged in both product.

TABLE 1

Resonance Band (cm^{-1})	Absorbance	
	Copolymer 1	Copolymer 2
1725	1.000	0.752
910	0.830	0.818

The ratio for copolymer 1: $\frac{0.830}{1.000} = 0.830$

and for copolymer 2: $\frac{0.818}{0.752} = 1.088$

Furthermore a relative diminution was observed in the absorbances at 970cm^{-1} and 690cm^{-1}, due to the loss of the different types of carbon double bonds of copolymer 1.

The results of the different epoxidation reactions are shown in the Table 2.

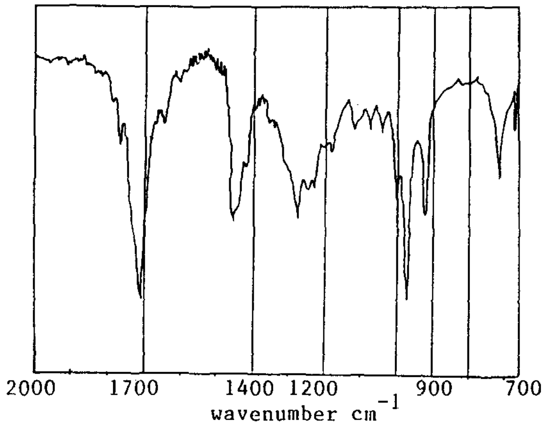

Figure 2
IR Transmission spectrum
of copolymer 1

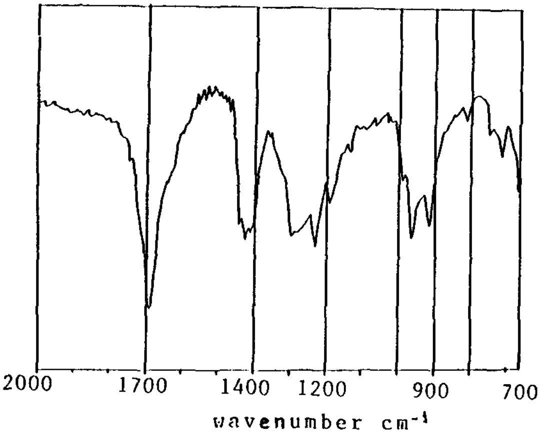

Figure 3
IR Transmission spectrum
of copolymer 2

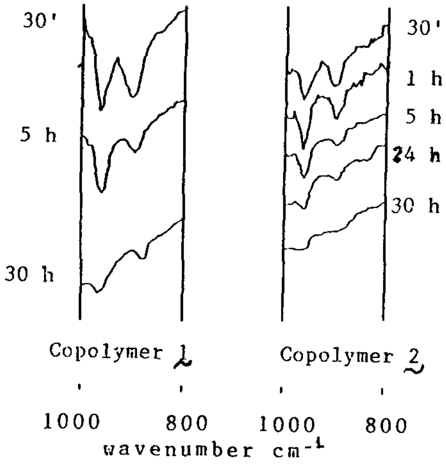

Figure 4
Disappearance of the
IR bands (1000-900 cm^{-1})

TABLE 2

Percarboxylic Acid	Catalyst	Temp. (°C)	Time (hs)	Oxirane Eq.$^{(d)}$
Benzoic	------	25	4	0 26
Acetic (a)	-----	25	4	0.24
Acetic (b)	1%H_2SO_4 (c)	50	2	----
Acetic (b)	Amberlite IRA-458	50	2	0.19
Acetic (b)	Amberlite IRA-120	50	2	0.06

(a): Previously synthesized (6).
(b): Generated in situ.
(c):96% wt/wt.
(d): Equiv./100g of resin.

The effect of temperature on copolymers 1 and 2 was followed by disappeaance of the band at 910 cm^{-1} by infrared spectroscopy (Figure 4).

A comparison between the two copolymers was carried out at 70°C by varying the time of heating. Copolymer 2 showed a significant percentage of disappearance (63%) after 24hs. This is not observed for copolymer 1 at the same period of time. This is due to an opening of oxirane groups during curing (7).

CONCLUSIONS

Copolymer 1 could be transformed to the corresponding epoxidized copolymer 2, using peroxyacids as oxidants. Higher oxirane group contents were obtained when peroxyacids were previously synthesized. The products were liquids with variable contents of oxirane group which can be cross-linked by heating at low temperatures (70-90°C) without catalysts.

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