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Copolymers from Castor Oil Prepolymers (COP). 1. Copolymerization of Acrylonitrile with COP

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Copolymers from Castor Oil Prepolymers (COP). 1. Copolymerization of Acrylonitrile with COP

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ABSTRACT

The copolymerization of castor oil prepolymer (COP) was attempted with vinyl monomers in the presence of a free radical initiator at 75°C. It was found that acrylonitrile copolymerizes with COP in good yield. The copolymers were yellow brown in color and were soluble in hot dimethylformamide. The percentage composition of the copolymers was determined by the nitrogen of the copolymers. Their reactivity ratios were determined to be $r_1 = 0.53$, $r_2 = 1.53$.

INTRODUCTION

Recently [1] it has been found that a useful rubberlike material is obtained by vulcanizing a castor oil prepolymer (COP) in the presence of sulfur and a suitable accelerator. The COP is prepared by reacting castor oil with a dibasic acid which is derived from castor oil itself, such as sebacic acid. The rubber from this prepolymer has little commercial value as it has a low tensile strength (286 psi) in comparison to natural rubber which has over 1500 psi. In order to improve the properties of the rubber, copolymerization of COP with a number

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of monomers was tried. It has been found that it copolymerizes with acrylonitrile. This paper deals with its copolymerization.

EXPERIMENTAL

Material

Acrylonitrile (EDH) was distilled and the fraction boiling at 76.5°C was collected in a dark container after drying over anhydrous sodium sulfate.

Benzoyl peroxide of reagent grade was crystallized twice in chloroform.

Solvents such as dimethylformamide and methanol were distilled before use.

The COP was prepared as mentioned in a Pakistan patent application [1] in which castor oil is reacted with a dibasic acid such as sebacid acid which was derived from castor oil itself in the presence of a catalyst (p-toluene sulfonic acid) at temperatures up to 180°C. A highly viscous COP was obtained.

All the copolymerizations were carried out in sealed tubes. The required amount of acrylonitrile and COP was transferred through a long stem funnel into the reaction tube kept at 0°C. To this, 0.005 g (0.1%) benzoyl peroxide was added and the tubes were then sealed. The reaction tubes were heated in a shaking bath at 75°C for 30 min. After the required time, the tubes were cooled and then broken open. The copolymer thus prepared was separated with methanol. It was a slightly brown to brownish precipitate and was soluble in hot dimethylformamide. Copolymers richer in COP content tend to become brownish. The copolymers decompose above 180°C.

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RESULTS AND DISCUSSION

The results of copolymerization of COP with acrylonitrile using benzoyl peroxide as a catalyst at 75°C are listed in Table 1.

As shown in Table 1, COP copolymerizes with acrylonitrile more readily. This is also apparent from the nitrogen analysis of the copolymers which ranges from 6.5 to 22.16% depending on the concentration of initial acrylonitrile used. These copolymers were not rubbery but brittle even when the percentage composition of acrylonitrile was as low as 10% of the total copolymer. The differences in the percentage of nitrogen may be due to the attachment of COP in the growing polymer chain of polyacrylonitrile, showing that the product is a copolymer. Infrared spectrum studies also support the results. The strong absorption band at 2280 cm^{-1} of nitrogen is quite distinct while the band at 3020 cm^{-1} shows the appearance of an ester group.

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TABLE 1. Copolymerization of Acrylonitrile (AN) and Castor Oil Prepolymer (COP) Using 0.1% Benzoyl Peroxide as Initiator at 75°C for 30 min

	Monomer in feed		Monomer in copolymer			Analysis (%)		
Sample	AN (g)	COP (g)	AN (g)	COP (g)	Conversion (%)	H	C	N
1	4.50	0.50	0.39	0.08	9.44	6.50	67.73	22.16
2	4.00	1.00	0.46	0.30	15.20	6.46	68.70	16.03
3	3.50	1.50	0.54	0.48	20.40	8.13	69.94	14.03
4	2.50	2.50	0.23	0.71	18.80	9.25	69.51	6.50
5	1.50	3.50	0.24	0.73	19.40	9.31	70.79	6.64

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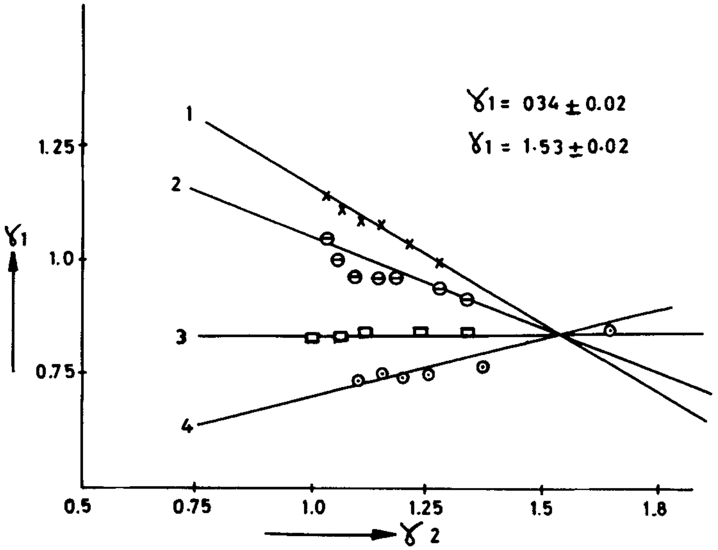

FIG. 1. Mayo and Lewis plot of r_1 against r_2 for copolymerization of acrylonitrile and COP.

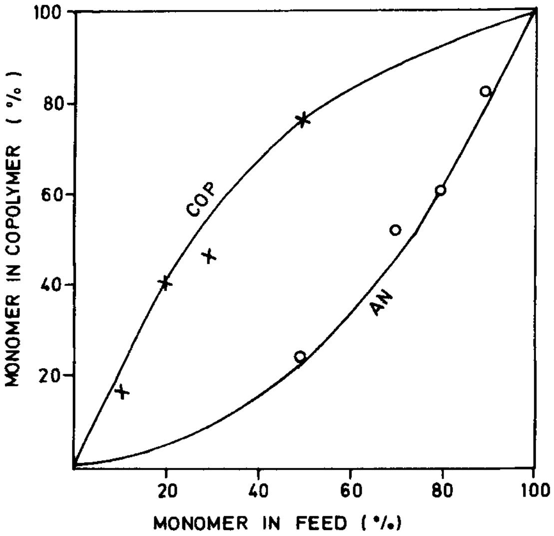

FIG. 2. A plot of percentage of monomer in copolymer versus percentage of monomer in feed.

The monomer reactivity ratios of the copolymer were determined by the method of Mayo and Lewis [2]. The r_1-r_2 plots are shown in Fig. 1. The values of r_1 (AN) and r_2 (COP) obtained by this method are 0.35 and 1.53, respectively. These values are quite consistent with the values of other acrylonitrile copolymers such as AN-methyl acrylate and AN-acrylic acid copolymers [3-5]. In the case of the monomer pair AN-methyl acrylate, the reactivity ratio of AN is 0.15 ± 0.03 while that of methyl acrylate is 1.05 ± 0.4. In the case of the AN-acrylic acid system, the reactivity ratios are 0.13 ± 0.02 and 6.0 ± 2.0, respectively.

The copolymer composition curve is shown in Fig. 2. It is apparent from these results that the percentage composition of acrylonitrile in the copolymer is quite consistent to the comonomer feed, which also shows more reactivity of acrylonitrile in this system.

The copolymers were not of much commercial value since they were brittle and the properties were more similar to those of polyacrylonitrile. The copolymer of acrylonitrile with a number of other monomers, especially monomers having a hydroxyl group, have also been reported to be dominated by acrylonitrile [5].

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