

COPOLYMERS OF CASTOR OIL PREPOLYMER

Part III. Copolymerization of Acrylic Acid with COP

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A study of copolymerization of castor oil prepolymer (COP) with acrylic acid has been carried out at 75° using benzoyl peroxide as inhibitor. It is found that good yields of copolymers are obtained at high feed of COP. The copolymers of low molecular weight decreasing with increasing concentration of acrylic acid are obtained. The intrinsic viscosities of copolymers are 0.039 to 0.074 dl/g. The copolymer obtained is soft rubbery type.

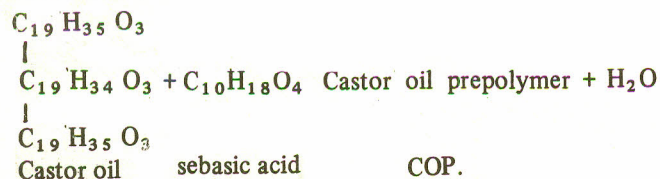
INTRODUCTION

Some vinyl monomers copolymerize with castor oil prepolymer (COP) in the presence of radical initiator. Castor oil prepolymer (COP) is obtained by treating castor oil with dibasic acid derived from castor oil itself such as sebacic acid in the presence of catalyst like *p*-toluene sulphonic acid. Rubber from COP is obtained, though it has little commercial value [1]. In our earlier publications we have already reported the copolymerisation of acrylonitrile [2] and styrene [3] with COP. The copolymers were not rubbery material but found brittle. Surprisingly COP inhibits the rate of polymerization of vinyl acetate instead of forming copolymer [4]. The induction period of polymerization of vinyl acetate increases with the increase in the concentration of COP. Some other vinyl monomers like acrylic acid and methyl methacrylate have been tried to copolymerise with COP. This paper deals with the copolymerization of acrylic acid with COP using benzoyl peroxide as initiator.

EXPERIMENTAL

Materials. Acrylic acid (Sealze Hannover) was distilled and the fraction boiling at 141° was collected. Solvents like methanol, acetone, chloroform, DMF, Tetrahydrofurane and dioxane were distilled before use.

Castor oil prepolymer (COP) was prepared [1] by treating castor oil with sebacic acid in the presence of a catalyst such as *p*-toluene sulphonic acid. The reaction will be as follows:-



The prepolymer so obtained is a viscous substance with a molecular weight of 1116, and density of 1.05 gm/ml. The elementary analysis of castor oil prepolymer was carried out, and the calculated values of C, H and O were found around its observed values:

Calculated values	Observed values
C 72.04 %	70.96 %
H 10.75 %	10.84 %
O 17.21 %	18.2 %

Benzoyl peroxide of reagent grade was twice recrystallised in chloroform.

Procedure of Copolymerization. The copolymerization was performed in sealed pyrex tubes. A weighed amount of acrylic acid and COP were added in the reaction tubes already containing 0.1 % benzoyl peroxide (0.005 gm). The reaction tubes were heated at 75° for 25 mints. After required reaction time, the tubes were broken open. The resulting product when precipitated out with methanol, was found soluble in hot water. It swelled in hot dioxane and tetrahydrofurane. Very small amount of the product was soluble in these solvents. It was a yellowish substance, which decomposed into light brown colour at 175° and reddish brown upto 300°.

The IR spectra of the product was also recorded to ascertain the product as a copolymer. The intrinsic viscosity of all copolymer samples was measured at 25° using Ostwald's viscometer. Distilled water was used as a solvent.

RESULTS AND DISCUSSION

The results in detail for the copolymerization of acrylic acid with COP are given in Table 1. The compositions of the resulting product of the four samples

Table 1. Copolymerization of acrylic acid with COP using 0.1 % benzoyl peroxide as initiator at 75° for 25 mints.

Samples No.	Monomer in feed		Conversion %	Intrinsic* viscosity dl/g	Analysis			
	Acrylic acid COP				C %	H %	O %	Ash %
	g	g						
1.	4.40	0.60	37.00	0.039	48.76	6.47	44.77	0.018
2.	3.70	1.30	42.10	0.059	50.97	7.20	41.83	0.137
3.	3.40	1.60	45.00	0.068	52.41	7.11	40.48	0.000
4.	2.30	2.70	50.40	0.074	56.56	7.90	35.54	0.008

*Viscosity of copolymer samples is measured in distilled water at 25°.

were carried out for carbon, hydrogen and oxygen. The elementary analysis showed the percentage of carbon and hydrogen ranging from 48.76 to 56.56 and 6.47 to 7.90 respectively whereas polyacrylic acid respectively contained carbon and hydrogen as 50% and 5.35 %. On the other hand the percentage of carbon and hydrogen in COP was 70.96 and 10.84, respectively. These variations in percentage of carbon and hydrogen were found amongst the product, polyacrylic acid and COP revealed attachment of COP molecules in the growing polymer chain of polyacrylic acid and that the product was obviously a copolymer. This is further supported by the fact that polyacrylic acid is soluble in dioxane, water, aqueous solutions of NaCl, aqueous solution of NaOH, DMF, alcohol whereas COP is soluble in alcohol. But the product was found soluble in hot water and partially in acetone and alcohol. It swelled in hot DMF, dioxane, tetrahydrofurane etc. The infrared spectrum studies also supported the results of the presence of ester, absorption band appearing at 3600 cm^{-1} wave number and $-\text{COOH}$ absorption band at 1775^{-1} provided further evidence that a copolymer has been found.

In Fig. 1 percentage oxygen is plotted against COP concentration which shows that the amount of oxygen is decreased from 44.77 to 35.54 % with increasing concentration of COP. Polyacrylic acid contains 44.45 % oxygen whereas COP contains 18.2 % oxygen suggesting that COP molecules are incorporated in the copolymer chain and the molecules of acrylic acid enter in the growing polymer chain slowly. Hence the resulting copolymer carries small chain of polyacrylic acid. It is also evident from the study of intrinsic viscosity of dilute solutions in hot water of copolymer samples. Although the intrinsic viscosity of copolymer samples increases with increase in concentration of COP but it lies in between 0.039 to 0.074 dl/g.

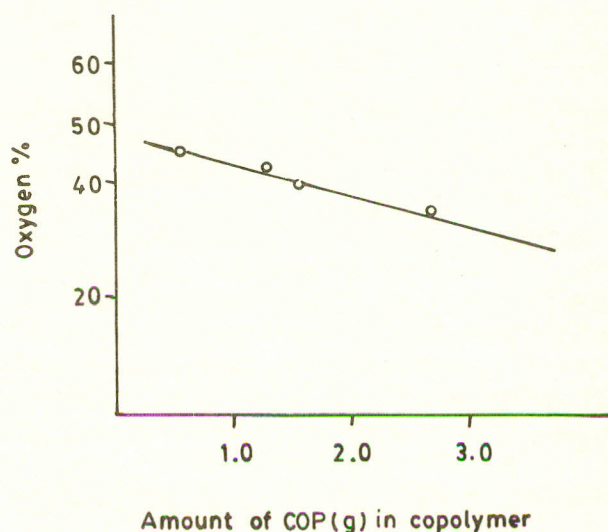


Fig. 1. A plot of oxygen % against amount of COP (g) in copolymer. This indicates that a copolymer of very low molecular weight is formed. Acrylic acid itself on polymerization gives polyacrylic acid of higher molecular weight which may be in three hundred thousand (e.g. 315000) or more [5].

It is evident from Table 1 that percentage conversion into copolymer increases with increase in concentration of COP on the pattern of copolymerization of acrylonitrile and COP. Acrylonitrile also copolymerizes with COP in good yield [2]. The copolymers of acrylonitrile and styrene with COP are brittle, while the copolymer of acrylic acid with COP is not brittle but is a soft rubbery type substance.

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