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Copolymers from Castor Oil Prepolymers (COP). 2. Copolymerization of Styrene with COP

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ABSTRACT

A study of copolymerization of castor oil prepolymers (COP) with styrene has been made at 75°C using benzoyl peroxide as initiator. It has been found that good yields of copolymers (high molecular weight $\overline{M}_n = 123{,}989$) are obtained at a low concentration of COP. With an increasing concentration of COP in the binary mixture, copolymers with decreasing molecular weight are obtained. This is explained as due to presence of a high percentage of oxygen (from COP) in the system which is acting as a chain transfer agent.

INTRODUCTION

In our earlier paper [1] the copolymer of acrylonitrile with castor oil prepolymer (COP) was investigated. It was found that acrylonitrile copolymerizes with COP in good yield. These copolymers are brittle materials even when the percentage composition of acrylonitrile is as low as 10% of the total copolymer. The castor oil prepolymer was obtained [2] by reacting castor oil with a dibasic acid derived from castor oil itself in the presence of a catalyst p-toluene sulfonic acid at 180° C. In another publication the inhibition effect of COP on bulk polymerization of vinyl acetate was observed. The induction period of polymerization of vinyl acetate increased with an increasing concentration of COP [3].

This paper deals with the copolymerization of styrene and COP using benzoyl peroxide as initiator.

EXPERIMENTAL

Materials

1. Styrene (E. Merck) was first washed with sodium hydroxide to remove the inhibitor and then dried over anhydrous calcium chloride. Finally, it was distilled with hydroquinone to avoid homopolymerization of styrene. The fraction of the monomer boiling at 146-150° C was collected.
2. Castor oil prepolymer was prepared according to the procedure stated elsewhere [2].
3. Reagent grade benzoyl peroxide was twice recrystallized in chloroform.
4. Reagent grade methanol, dimethylformamide, and benzene were distilled before use.

Procedure of Copolymerization

All copolymerization reactions were conducted in sealed glass tubes. Known amounts of styrene and castor oil prepolymer were transferred to the tubes containing benzoyl peroxide (0.005 g). The tubes were sealed by constriction and heated at 75° C for 4 h. After the required reaction time the tubes were broken open and the resulting product was separated out by the benzene-methanol precipitant system. The product thus obtained was found soluble in benzene and hot dimethylformamide. It is a white yellowish substance. It decomposes at 145° C and turns brown at 160° C. Above this temperature it becomes black. The IR spectra of styrene, COP, and the product showed the substance to be a copolymer.

The viscosity of a dilute solution of copolymer prepared in hot benzene was measured at 30 ± 0.1 using an Ostwald-type viscometer.

The composition of the copolymer was determined by analyzing the copolymer samples for carbon, hydrogen, and oxygen.

RESULTS AND DISCUSSION

The detailed results of the copolymerization of styrene and COP are summarized in Table 1.

TABLE 1. Copolymerization of Styrene and COP Using 0.1% Benzoyl Peroxide as Initiator at 75°C for 4 H

No.	Monomer in feed: Styrene (g)	Monomer in feed: COP (g)	Weight of copolymer obtained (g)	Analysis (%): C	Analysis (%): H	Analysis (%): O
1	4.00	1.00	3.85	89.82	8.23	1.95
2	3.60	1.40	3.50	88.03	9.04	2.93
3	2.70	2.30	2.66	88.20	8.40	3.40
4	1.50	3.50	1.08	82.68	9.16	8.10

Elementary analyses of the resulting product of the four samples of the binary mixture of styrene and COP were carried out for hydrogen, carbon, and oxygen. The four samples contain 1.95-8.1% oxygen wereas COP contains 18.2% oxygen. This suggests an attachment of COP molecules in the growing polymer chain of polystyrene and that the product is obviously a copolymer. This is further supported by the fact that polystyrene and COP are soluble in benzene and alcohol, respectively, while the copolymer is also soluble in hot dimethylformamide. IR spectral studies of copolymers of styrene and COP were compared with the spectra of COP and polystyrene. The presence of an ester absorption band at 3000 cm^{-1} and a C=C (aromatic ring) absorption band at 1625 cm^{-1} provides further evidence that a copolymer has been formed.

Since the amount of oxygen in the copolymer increases with an increasing concentration of COP as shown in Fig. 1, the copolymerization of a binary mixture of styrene and COP gives an initial product which is virtually pure polystyrene. The rate of increase in the amount of the product with styrene (Table 1) also provides evidence that styrene enters the polymer chain more rapidly than COP. Hence the addition of COP molecules to the growing polymer chain of polystyrene is very slow.

The number-average molecular weight $\overline{M}_n$ of copolymer was calculated by using the relationship [4]

$$[\eta] = 0.97 \times 10^{-4}\ \overline{M}_n^{\,0.74}$$

where $[\eta]$ is the intrinsic viscosity of the copolymer solution obtained by plotting η_{sp}/c against c. Here η_{sp} is the specific viscosity and c is the concentration of the solution prepared in benzene. The intrinsic viscosity of the copolymer samples was found in the range from 0.20 to 0.57 dL/g. These intrinsic viscosity values give $\overline{M}_n$ as

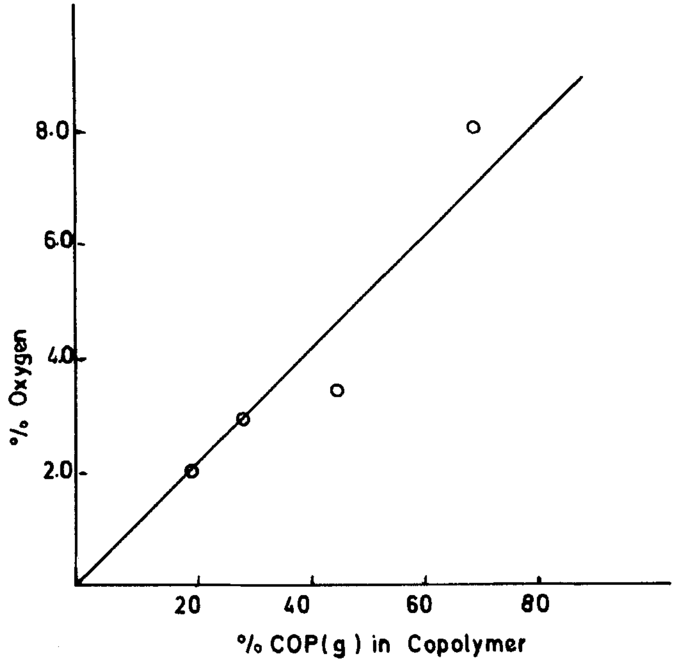

FIG. 1. A plot of % oxygen against % COP (g) in copolymer.

TABLE 2. Intrinsic Viscosity [η] and Number-Average Molecular Weight $\overline{M}_n$ of Copolymer Sample of Styrene and COP

No	[η] (dL/g)	$\overline{M}_n$
1	0.57	123,989
2	0.43	84,716
3	0.29	49,750
4	0.20	30,111

30,111 to 123,989. The results are shown in Table 2. It is evident (from Table 2) that the $\overline{M}_n$ of the copolymer decreases with the increase in the concentration of COP in the copolymer. This results in the high percentage of oxygen in the system which is responsible for the decrease in molecular weight of the copolymer. Since oxygen is known to act as a chain transfer agent as well, its high percentage in the system also degrades the polystyrene molecule [5-7].

The copolymers are not of much commercial importance because they are brittle. The same brittleness was also found in the copolymers of acrylonitrile and COP [1].

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