Copolymers from Castor Oil Prepolymers (COP). 4. Copolymerization of Methyl Methacrylate with COP

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ABSTRACT

The copolymerization of castor oil prepolymer (COP) with methyl methacrylate (MMA) has been accomplished at 75°C using a free radical initiator. The monomer reactivity ratios of MMA (r_1) and COP (r_2) were determined to be $r_1 = 3.04$ and $r_2 = 0.605$. With an increasing concentration of COP in the binary mixture, copolymers with decreasing molecular weight were obtained. The copolymers obtained were powdery substances soluble in many organic solvents.

INTRODUCTION

The copolymers of castor oil prepolymer (COP) with acrylonitrile [1], styrene [2], and acrylic acid [3] were reported earlier. These copolymers were prepared in order to improve the properties of rubber obtained by vulcanizing COP in the presence of sulfur and a suitable accelerator since it has low tensile strength in comparison with natural rubber. The copolymers obtained by copolymerizing with acrylonitrile and styrene were brittle, while copolymerization of COP with acrylic acid results in a soft, rubbery-type material. Some other

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monomers (e.g., vinyl acetate [4] and methyl methacrylate) were also copolymerized with COP. It was observed that COP inhibits the polymerization of vinyl acetate instead of forming copolymer whereas methyl methacrylate copolymerizes with COP. This paper deals with the copolymerization of COP with MMA using benzoyl peroxide as the catalyst.

EXPERIMENTAL

Materials

Methyl methacrylate (BDH) was washed with NaOH to remove inhibitor and dried over $CaCl_2$. It was then distilled, and the fraction boiling at 99 to 100.5°C was collected. Castor oil prepolymer (COP) was prepared according to the procedure given elsewhere [5]. Reagent grade methanol chloroform, acetone, DMF, and toluene were distilled before use. Reagent grade benzoyl peroxide was twice recrystallized in chloroform.

Method of Copolymerization

Reactions were carried out in sealed tubes. Methyl methacrylate and COP in different ratios, as given in Table 1, were transferred to reaction tubes containing 0.1% (0.005 g) benzoyl peroxide. The tubes were sealed. The reaction was conducted for 90 min at 75°C in a water bath. At the end of the experiment a viscous syrupy liquid was obtained. The resulting product was separated by the acetone-methanol solvent precipitant system. The product thus obtained was found to be soluble in DMF, acetone, toluene benzene, and chloroform. It is a white powdery substance. It begins to melt at 155°C and turns brown above 200°C. The IR spectra of COP and the product showed that the substance is a copolymer. The viscosity of dilute solutions of the copolymer prepared in acetone was measured at $30 \pm 0.1°C$ using an Ostwald-type viscometer. The copolymer samples were analyzed for C, H, and the OCH_3 group.

Determination of Methoxyl Group

The methoxyl ($-OCH_3$) group was determined in the form of an ester by treating the copolymer sample with boiling hydroiodic acid using a modified Clark apparatus [6]. This treatment split $-OCH_3$ from the copolymer chain and converted it into methyl iodide. The methyl iodide so formed was determined iodometrically. The method was standardized by the analysis of freshly prepared poly(MMA). The accuracy of the determination was 0.3%.

TABLE 1. Copolymerization of Methyl Methacrylate with Castor Oil Prepolymer (COP) Using 0.1% Benzoyl Peroxide as Initiator at 75°C for 90 min

Sample	Monomer in feed		Conversion (%)	Analysis			Rate of polymerization $R_p \times 10^{-5}$ mol/L/s	
	MMA (g)	COP (g)		C%	H%	–OCH$_3$%	MMA	COP
1	4.67	0.63	79.0	60.71	8.21	29.10	123.7200	0.7237
2	4.08	0.92	77.0	60.77	8.39	27.50	121.6040	1.3868
3	3.19	1.81	58.4	61.36	8.44	24.62	84.2047	1.9554
4	2.65	2.36	39.4	61.70	8.46	23.40	54.5287	1.5871

RESULTS AND DISCUSSION

The detailed results for the copolymerization of COP and methyl methacrylate using benzoyl peroxide as initiator at 75°C are shown in Table 1.

Estimation of the resulting product of four samples of binary mixtures of poly(MMA) and COP were carried out for C, H, and the $-OCH_3$ group. The four samples of the product contain the methoxyl group (23.4 to 29.1%). On the other hand, poly(MMA) contains 30.7% of the $-OCH_3$ group. This difference in the percentage of the $-OCH_3$ group among the product and poly(MMA) shows the attachment of COP molecules in the growing polymer chain of poly(MMA). Elementary analysis for C and H of the product is 60.71 to 61.7% and 8.21 to 8.46%, respectively. On the other hand, poly(MMA) and COP 60 and 70.96% C, respectively, whereas poly(MMA) contains 8% H and COP contains 10.84% H. These differences in percentage of C, H, and the $-OCH_3$ group among the product, poly(MMA), and COP show the entrance of COP molecules in the growing polymer chain of poly(MMA) and that the product is obviously a copolymer. Further, the product is soluble in DMF, acetone, benzene, toluene, and chloroform, while poly(MMA)

TABLE 2. IR Spectra of COP, MMA, and Copolymer[a]

COP cm^{-1} frequency	MMA cm^{-1} frequency	Product (copolymer) cm^{-1} frequency
3500 (s)	2960 (s)	3400 (s)
3000 (s)	2400 (w)	2900 (m)
1800 (m)	1960 (w)	1700 (s)
1730 (m)	1700 (s)	1420 (w)
1650 (m)	1440 (m)	1370 (m)
1560 (m)	1380 (w)	
1500 (w)	1120-1240 (m)	1220 (m)
1420 (w)	1060 (w)	1150 (w)
1280 (m)	960 (m)	1020 (w)
1210 (w)	825 (w)	900 (w)
1130 (m)	740 (s)	
840 (m)		

[a]S = strong, m = medium, and w = weak.

and COP are soluble in acetone, chloroform, and alcohol. The solu-
bility of the product in the above-mentioned solvents may be more evi-
dence in support of the elementary analysis. IR spectral studies of
the product and polymers were also carried out (Table 2). It is gen-
erally observed that the spectra of the polymers are much simpler
than the spectra of the monomer. This is due to the fact that the degree
of freedom of vibration is restricted in the polymer and copolymer. How-
ever, the general patterns of the spectra of the polymer, copolymer, and
monomers remain the same. The spectra of the copolymer, as a rule,
show the addition on commutative behavior of its monomers. The IR
spectra of the product in Table 2 show lesser bands than the spectra of
poly(MMA) and COP. The presence of carbonyl absorption bands at
1700 cm^{-1}, ester absorption band at 2900 cm^{-1}, and $C-CH_3$ (methyl)
absorption band at 1370 cm^{-1} provides definite proof that a copolymer
has been formed.

The monomer reactivity ratios of methyl methacrylate (r_1) and COP
(r_2) are determined by using the integrated form of the equation of
Mayo and Lewis [7]. In Fig. 1, r_1 values have been plotted against r_2
values. The values of r_1 and r_2 obtained from this plot are 3.04 and
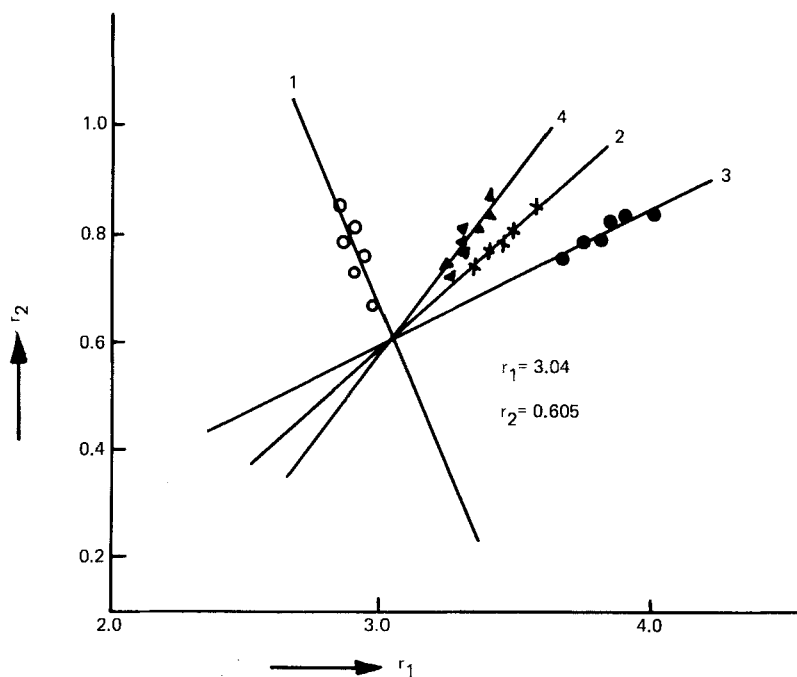

FIG. 1. Mayo and Lewis plot of r_2 against r_1 for the copolymeriza-
tion of MMA and COP.

0.605, respectively. Since one reactivity ratio is greater than unity (r_1 = 3.04) and the other is less than unity (r_2 = 0.605), the present copolymer system is nonazeotropic. As both r_1 and $1/r_2$ are greater than unity, both radicals prefer the same monomer, i.e., MMA. The rate of polymerization of MMA increases with increasing concentration of the monomer. Estimation of the product shows that the percentage of methoxyl group ($-OCH_3$) in the copolymer chain decreases with an increase in the concentration of COP. All this evidence indicates that MMA is more reactive than COP, although COP is already in the process of polymerization. At the initial stages, homopolymerization of MMA takes place, and then MMA and COP are copolymerized. In the case of the copolymerization of AN and COP [1], the reactivity ratio values of COP (1.53) are greater than the reactivity ratio values of AN (0.35), indicating that MMA is more reactive toward COP than acrylonitrile.

The number-average molecular weight $\overline{M}_n$ of copolymer samples was calculated by using the following intrinsic viscosity $[\eta]$ and molecular weight relationship [8]:

$$[\eta] = 7.7 \times 10^{-5} \, \overline{M}_n^{\,0.7}$$

The intrinsic viscosity of dilute solutions of copolymer samples prepared in acetone was determined by plotting η_{sp}/c vs c, where η_{sp} is the specific viscosity and c is the concentration of the solution expressed as a percentage. Viscosity was measured at 30°C. The intrinsic viscosity of the copolymer sample was found to be in the range 0.385 to 0.48 dL/g which gives the molecular weight as 192,416 to 263,676. The results are shown in Table 3. The intrinsic viscosities of copolymer samples prepared at different monomeric ratios are very close. The molecular weight of the copolymer chain decreases with an increasing concentration of COP, although very little. This indicates that COP also acts as a chain transfer agent. It was also observed in COP-styrene copolymerization [2] that with an increasing concentration of COP in the binary mixture, copolymers with decreasing molecular weight were obtained. This was explained as being due to the presence of a high percentage of oxygen (from COP) in the system, acting as a chain transfer agent. In the case of acrylic acid-COP copolymerization [3], the molecular weight decreases with an increasing concentration of acrylic acid, and a copolymer of lower molecular weight was obtained.

The copolymer obtained is a white powdery substance. A sheet of copolymer (6 cm × 2.0 cm × 0.4 cm) was cast at 155°C under a pressure of 1000 lb. The sheet was yellowish and transparent. The bending strength of the sheet was 1.04 kp/cm^3, which is comparatively lower than the bending strength of a sheet prepared from poly(MMA). The color of the sheet may be due to the attachment of COP molecules to the polymer chain of poly(MMA).

TABLE 3. Intrinsic Viscosity $[\eta]$ and Number-Average Molecular Weight $(\overline{M}_n)$ of Copolymer Samples Prepared from Methyl Methacrylate and COP

Sample	$[\eta]$ (dL/g)	$\overline{M}_n$
1	0.480	263676
2	0.450	240455
3	0.410	210511
4	0.385	192416

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