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Synthesis of functional unsaturated polyester by using rare earth catalysts

I. Copolymerization of epichlorohydrin with maleic anhydride in the presence of $Y(P507)_3$-$Al(i\text{-}Bu)_3$

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SUMMARY

Ring-opening copolymerization of epichlorohydrin(ECH) with maleic anhydride(MAn) was catalyzed by yttrium phosphonate in combination with triisobutylaluminum for the first time to give almost alternate copolymer, functional polyester. The yield and composition of the copolymer were affected by the reaction conditions, especially the initial monomer charge ratio. The overall activation energy of the copolymerization was estimated to be 19.0Kcal/mol. Evidence for the structure of ECH-MAn copolymer prepared was obtained by IR and ^{1}H-NMR.

INTRODUCTION

Although alternating copolymerization of cyclic acid anhydride and epoxides to form polyester had been reported using tertinary amine[1], metal salt[2] or organometallic compound[3] as catalysts, the copolymerizations of functional group-containing epoxides such as epichlorohydrin with cyclic acid anhydride were still rather undeveloped.

On the other hand, rare earth coordination catalysts were very effective for the ring-opening polymerization of epoxides, such as ethylene oxide[4], propylene oxide[5], epichlorohydrin[6] etc. The corresponding polymers can be prepared under mild conditions, with high rate, high degree of conversion, high molecular weight and good stereo-regularity. Furthermore, introducing functional group into the polymer was favoured for modifying of polymer by grafting or reacting. This challenges our interest in exploring these new catalyst for the ECH-MAn copolymerization.

In this paper, the ring-opening copolymerization of MAn with ECH by using rare earth catalyst has been reported for the first time, with emphasis on the influence of reaction conditions on the copolymerization in the presence of $Y(P507)_3$-$Al(i\text{-}Bu)_3$ ($P507= RO\text{-}\underset{R}{P}OO\text{-}$, $R=CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}$).

EXPERIMENTAL

Materials. Epichlorohydrin(ECH) was refluxed over CaH_2 and distilled before use. Maleic anhydride(MAn) was recrystallized from chloroform and then dried under reduced pressure. All solvents were purified by the ordinary methods.

Catalyst and Copolymerization. $Y(P507)_3$ was synthesized according to the reference[7]. The solution of $Y(P507)_3$-$Al(i\text{-}Bu)_3$ in toluene was prepared as described previously[6]. Ring-opening copolymerization of ECH with MAn was conducted in a sealed-tube under dry nitrogen. After a period of time, the reaction mixture was precipitated by ethanol containing 5% HCl. The resulting copolymer was washed with ethanol for several times, and then dried in vacuo at room temperature. The conversion was calculated by the following equation:

$$\text{Conversion}(\%)=\frac{\text{copolymer obtained(g)}}{\text{ECH used(g)+MAn used(g)}}\times 100$$

Analysis of the MAn-ECH Copolymer. IR spectra of the copolymers were recorded on a Shimadzu IR-470 spectrophotometer. ^1H-NMR of the copolymer in $CDCl_3$ was measured on a JEOL FX-90Q NMR at room temperature by using tetramethylsilane(TMS) as internal reference. The intrinsic viscosity of the copolymer was measured in chloroform at 30°C with a Ubbelohde-type viscometer(c=0.37g/dl).

RESULTS AND DISCUSSION

Copolymerization of MAn and ECH in Different Solvents

It has been found that the ring-opening copolymerization of MAn with ECH can be carried out in toluene, benzene, cyclohexane, chloroform, dichloromethane, 1,4-dioxane and 2-butanone by using $Y(P507)_3$-$Al(i\text{-}Bu)_3$ as catalyst. The copolymers obtained are yellow rubbery solid, soluble in chloroform, dichloromethane, THF and 1,4-dioxane, but insoluble in methanol, ethanol, petroleum ether and cyclohexane. In cyclohexane, copolymer was precipitated during the copolymerization reaction. Table 1 shows the results of copolymerization conducted in different solvents. As seen from the data, it can be found that the conversion of copolymerization was very high. And also, the monomer conversion was decreased with the increasing of solvent polarity. But for 1,4-dioxane, it gave a little lower yield even though its dielectric constant was close to those of benzene and toluene. This may caused by the electron-donor property of the solvent which competed with ECH in coordinating with the catalyst species, thus decreased the copolymer yield. The varying tendency of the copolymer yield agrees with a coordinate, not an ionic type of copolymerization.

Table 1. Ring-opening Copolymerization of ECH-MAn in Different Solvents[a]

solvent	dielectric constant	conv.%	$[\eta]$ $(10^{-2}dl/l)$
toluene	2.36	90	6.03
benzene	2.27	85	5.88
cyclohexane	2.02	89	5.02
2-butanone	ca.18	44	5.00
1,4-dioxane	2.21	64	5.94
dichloromethane	9.14	78	3.97

[a] ECH = MAn =1mol/l; Y =0.01mol/l; Al/Y=8; 75°C; 3h.

Effect of the Reaction Temperature

The ring-opening copolymerization of MAn with ECH was carried out at 30°C, 50°C and 70°C. The rate of the copolymerization reaction was found to increase remarkably with the rise of temperature. The values showed that the kp at 70°C was higher as much as 45 times than that at 30°C. From the plot of -lnkp to 1/T(Figure 1), the overall activation energy(Ea) was estimated to be 19.0Kcal/mol according to the Arrhenius' equation.

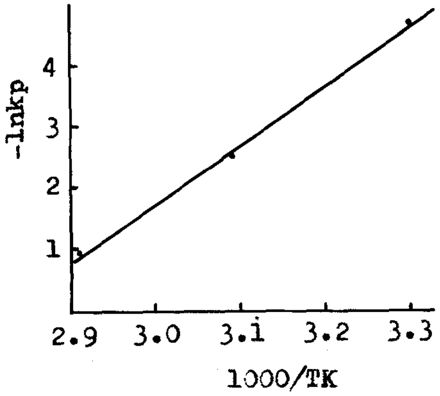


Figure 1. The plot of -lnkp to 1/T. Al/Y=8; Y=0.01mol/l; MAn /ECH =1; MAn =1mol/l; in toluene

Effect of the Initial Monomer Charge Ratio

Table 2. Effect of MAn / ECH on the Copolymerization[a]

MAn / ECH	conv.%	f(MAn)	f(ECH)
0.437	60.0	0.369	0.633
1.041	66.4	0.433	0.567
1.758	48.4	0.434	0.566

[a] Al/Y=8; Y =0.01mol/l; MAn + ECH =2mol/l; 60°C; 3.5h; in toluene

The initial monomer charge ratio affected not only on the catalytic activity but also the ester unit content of the copolymer obtained. As shown in Table 2, the monomer conversion of the copolymerization reaction increased with the increasing of MAn / ECH and a maximum value was found at MAn / ECH =1. The ester unit content of the copolymer was also increased with the increasing of MAn / ECH. The maximum content of MAn in copolymer chain (f(MAn)) reached 43% which showed the copolymer had almost alternating structure.

Structure of the MAn-ECH Copolymer

Figure 2 shows the IR spectrum of MAn-ECH copolymer prepared by the $Y(P507)_3$-$Al(i\text{-}Bu)_3$ system under the condition of Al/Y=8; Y =0.01mol/l; MAn =1mol/l; MAn / ECH =1; 60°C; 3.5h; in toluene. Strong absorption band at wavenumber 1720 cm^{-1} was due to the stretching vibration of C=O double bond. 1211 and 1157cm^{-1} absorptions were caused by the C-O-C stretching vibration in ester unit. Very weak absorption at 1118cm^{-1} meant a little C-O-C ether linkage existing in the copolymer chain. The absence of 1800-1850cm^{-1} absorption suggested that there was no MAn-MAn adjacent unit in the copolymer chain.

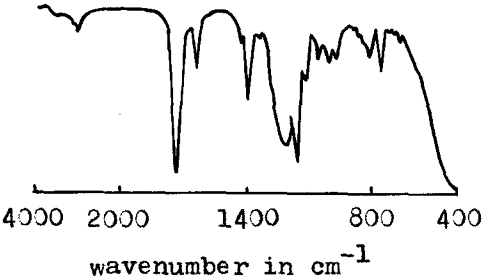
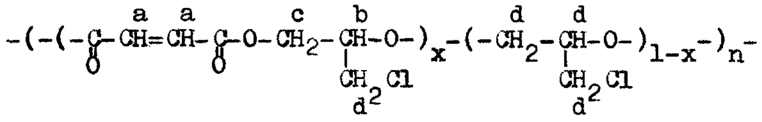


Figure 2. IR spectrum of the MAn-ECH copolymer

^{1}H-NMR spectrum of the copolymer so obtained is shown in Figure 3. The chemical shifts can be assigned by the following way: 6.24ppm(Ha), 5.25ppm(Hb), 4.42ppm(Hc), 3.77ppm (Hd).



$$-(-(-\underset{\underset{O}{\|}}{C}-\overset{a}{CH}=\overset{a}{CH}-\underset{\underset{O}{\|}}{C}-O-\overset{c}{CH_2}-\overset{b}{\underset{\underset{d^2}{CH_2Cl}}{\underset{|}{CH}}}-O-)_x-(-\overset{d}{CH_2}-\overset{d}{\underset{\underset{d^2}{CH_2Cl}}{\underset{|}{CH}}}-O-)_{1-x}-)_n-$$

where x is the average molar fraction of the ester unit, ie. alternating degree. The ester unit content of the copolymer (in mole) can be calculated according to the following equation:

$$x\% = \frac{5A(Hb) + 5A(Hc)}{3A(Hd) - 3A(Hc)} \times 100$$

Thus, the MAn content of the copolymer f(MAn)=x%/(1+x%). In Figure 3, f(MAn) was estimated to be 0.43 and it can also be found that there are absorptions in the range of 0.8-1.3ppm which are due to the $-CH_3$'s of end group. This means that the iso-butyl group in $Al(i\text{-}Bu)_3$ has been introduced into the copolymer chain in the initial step of the copolymerization reaction. The number-average molecular weight of a few samples estimated from the integral ratio of end group to main chains in ^{1}H-NMR was in the range of 2000 to 4000, in accordance with the results of GPC. The investigation on the mechanistic aspects and the copolymerization in the presence of other rare earth catalysts are in progress.

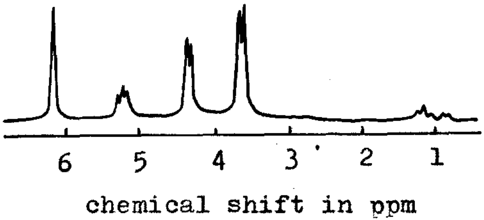


Figure 3. ^{1}H-NMR spectrum of the MAn-ECH copolymer

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