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CATIONIC COPOLYMERIZATION OF EPICHLOROHYDRIN WITH STYRENE OXIDE AND WITH CYCLOHEXENE OXIDE

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ABSTRACT

Cationic copolymerizations of epichlorohydrin (ECH) (chloromethyl oxirane) with styrene oxide (SO) (phenyl oxirane) and with 1,2-cyclohexene oxide (CO) (7-oxabicyclo [410] heptane) were carried out at 50°C by employing the salt triphenylmethyl hexachloroantimonate (HC) (Ph_3CSbCl_6) as initiator. NMR spectra before and after attempted extractions of the polymeric products indicated that the resulting polymeric products were true copolymers and not mixtures of the respective homopolymers. Monomer reactivity ratios for both pairs of comonomers were determined; for one pair the values were r_1(ECH) = 3.29, r_2(CO) = 0.16 and for the second pair r_1(ECH) = 0.57, r_2(SO) = 0.16.

INTRODUCTION

Cationic homopolymerizations of oxiranes have received considerable attention in the past as well as currently. Over the years, copolymerizations of different oxiranes and larger cyclic ether comonomers have been studied [1-3]. Because styrene oxide (SO) and 1,2-cyclohexene oxide (CO) have been of interest in our laboratory in connection with homopolymerization studies and because of the long time interest of industry in these monomers [4-10], we decided to determine the reactivity ratios of CO and SO with another more common oxirane, epichlorohydrin (ECH), also of interest in the polymer industry. Triphenylmethyl hexachloroantimonate (HC) was used as initiator.

There is limited information on the cationic copolymerization of SO and CO with ECH. As a part of a patent, Baggett and Pruitt [5] showed that SO and ECH copolymerize with a $FeCl_3$-propylene oxide catalyst. Triphenylmethyl hexafluoroantimonate was used to copolymerize SO with other cyclic ethers [6]. Movsumzade et al. [11] copolymerized CO with trimethylethylene oxide by using $TiCl_4$ as catalyst, yielding reactivity ratios of 1.28 and 0.85, respectively, at low conversions. For the system CO and ECH these same authors [11] found reactivity ratios were $r_1(CO) = 1.89$ and $r_2(ECH) = 0.15$. Blanchard et al. [12] copolymerized styrene oxide with propylene oxide in ethylene oxide by using BF_3 etherate as catalyst and 1,3-propandiol as cocatalyst.

EXPERIMENTAL

Reagents

Epichlorohydrin (Pfaltz and Bauer) and 1,2-cyclohexene oxide (PCR) were distilled under vacuum through a Snyder distillation column. Styrene oxide (Pfaltz and Bauer) was distilled under vacuum on a spinning band apparatus. Antimony pentachloride (J. T. Baker) was purified by saturating it with chlorine gas and then distilling it under reduced pressure [13]. Triphenyl chloromethane (Aldrich) was purified by crystallization after which it had a melting point of 110-113°C. Carbon tetrachloride (J. T. Baker) was distilled through a Snyder column.

Synthesis of HC (Ph_3CSbCl_6)

Purified triphenyl chloromethane (0.0235 mol) dissolved in CCl_4 (100 mL) was added to antimony pentachloride (0.0235 mol) also in CCl_4

(100 mL). The trityl salt which precipitated was filtered, washed with carbon tetrachloride, and dried in a vacuum oven overnight at 60°C.

Copolymerizations

A solution of the initiator in dichloromethane was added to the reaction tube, after which the latter was quickly connected to a vacuum line. After the solvent was removed, the comonomers were added at liquid nitrogen temperature and the reaction tube sealed under vacuum. It was then placed in a constant temperature bath with the provision of having the reaction tube rotated end over end, causing the contents to mix efficiently. The copolymerization period was 1 h, after which the tube was opened and the copolymerizing mixture poured into a large excess of methanol. The copolymers which precipitated in methanol were washed with methanol and freeze dried from frozen benzene solutions in the case of the ECH–CO copolymers. The copolymers of ECH–SO were freeze dried from a frozen CCl_4 solution at −30°C for 3 days. The number-average molecular weights of the copolymers were determined by vapor pressure osmometry in chloroform at 37°C. The copolymer compositions were determined from the T-60 NMR spectra of the copolymers. Copolymerizations were prepared at 50°C by using a total volume of 5 mL of comonomers and a concentration of initiator of 1×10^{-3} mol/L comonomer. All copolymerizations were run neat.

RESULTS AND DISCUSSION

Experimental data obtained for the copolymerization runs are shown in Tables 1 and 2.

Figure 1 is a typical NMR spectrum of an ECH–CO copolymer. The adsorptions in the range of 1–2 ppm represent the methylene protons in the CO residue. The adsorption at 3.2 ppm is assigned to the methine proton of the CO residue, and the adsorption at 3.5 ppm is associated with all the protons in the ECH residue.

Figure 2 is a typical spectrum of the copolymer of ECH and SO. The adsorption at 7.2 ppm represents all the aromatic protons. The adsorption at 4.3 ppm is assigned to the methine proton in the SO residue. The adsorption at 3.5 ppm is associated with all the protons in the ECH residue and the methylene protons in the SO residue.

NMR peak areas were used in the construction of a calibration curve

TABLE 1. Experimental Conditions and Results for the Epichlorohydrin–1,2-Cyclohexene Oxide Copolymerizations

	Charge composition				Copolymer composition		
Sample	M_1 (ECH), mol%	M_2 (CO), mol%	Polymerization temperature, °C	Yield, wt%	M_1, mol%	M_2 mol%	M_n
23-1	87.19	12.81	50	1.6746	59.9	40.1	5322
23-2	83.84	16.16	50	1.7556	53.6	46.4	5379
23-3	80.42	19.58	50	1.9376	49.6	50.4	5209
23-4	73.37	26.63	50	1.9616	38.6	61.4	3451
23-5	66.05	33.95	50	2.1031	30.4	69.6	2971
23-6	56.46	43.54	50	2.1929	25.2	74.8	1071
23-7	46.37	56.63	50	2.3133	20.5	79.5	781

TABLE 2. Experimental Conditions and Results for the Epichlorohydrin–Styrene Oxide Copolymerizations

Sample	Charge composition		Polymerization temperature, °C	Yield, wt%	Copolymer composition		M_n
	M_1 (ECH), mol%	M_2 (SO), mol%			M_1, mol%	M_2 mol%	
24-1	91.43	8.57	50	1.2655	72.0	28.0	12,717
24-2	85.33	14.67	50	1.5707	63.4	36.6	9,745
24-3	82.17	17.83	50	1.4555	61.0	39.0	9,779
24-4	77.39	22.61	50	1.3197	58.2	41.8	9,657
24-5	68.57	31.43	50	1.3125	55.9	44.1	8,035
24-6	45.00	55.00	50	1.4244	40.0	60.0	3,625
24-7	36.13	63.87	50	0.6508	35.2	64.8	3,367

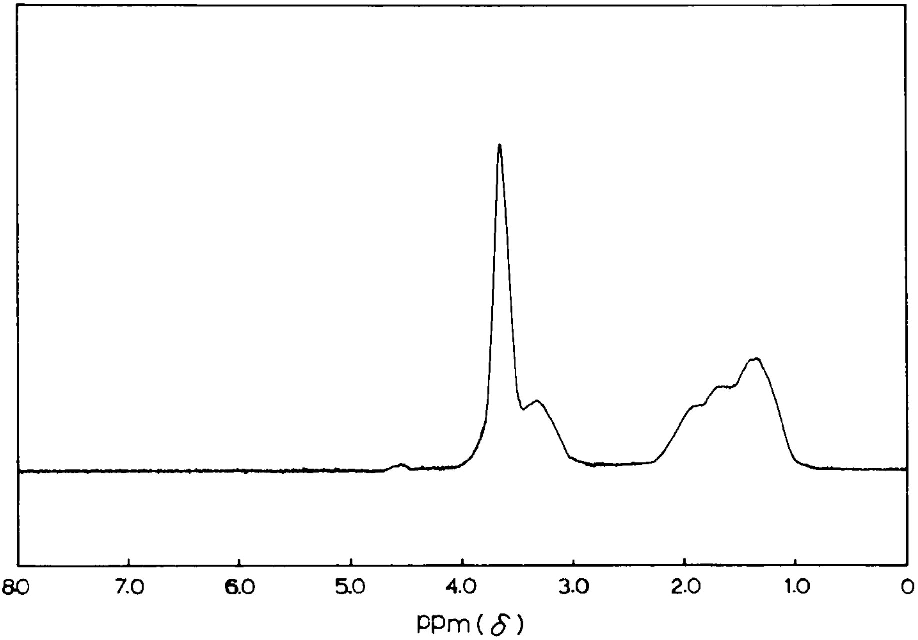


FIG. 1. Typical T-60 NMR spectrum of copolymer of cyclohexene oxide and epichlorohydrin.

which in turn was used to obtain mole percent of residue in the copolymers produced. A series of solutions of different compositions of the respective two homopolymers were made, and the NMR spectra of these mixtures were obtained. The ratios of the adsorption areas at 3.5 ppm and in the range 1–2 ppm for polyECH and polyCO were then plotted against the mole percent composition of one of the monomer residues of the mixture. Analysis of a copolymer consisted of determining the ratio from the NMR spectrum of the copolymer and applying it to the calibration curve to read the respective mole percent of the residue in the copolymer. For the calibration utilized in the analysis of the ECH-SO copolymers, the adsorptions at 7.2 and 3.5 ppm were used.

Once the copolymer compositions were determined, reactivity ratios were determined by the method of Kelen and Tüdös [14] to be r_1(ECH) = 3.29, r_2(CO) = 0.16 and r_1(ECH) = 0.57, r_2(SO) = 0.16. Figure 3 shows the relationship between copolymer composition and monomer charge composition. The ECH-CO system, which has a large r_2 (where

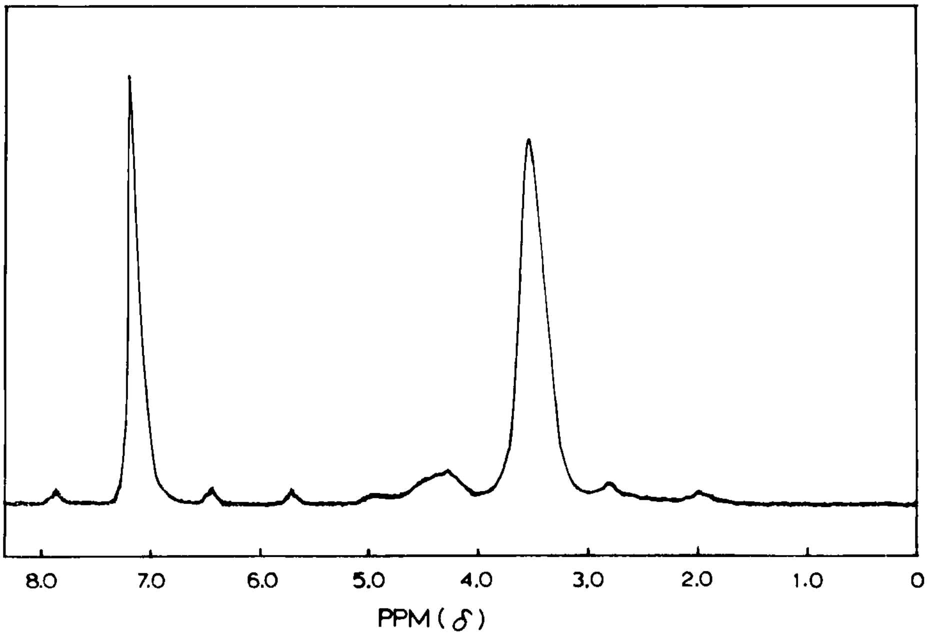


FIG. 2. Typical T-60 NMR spectrum of copolymer of styrene oxide and epichlorohydrin.

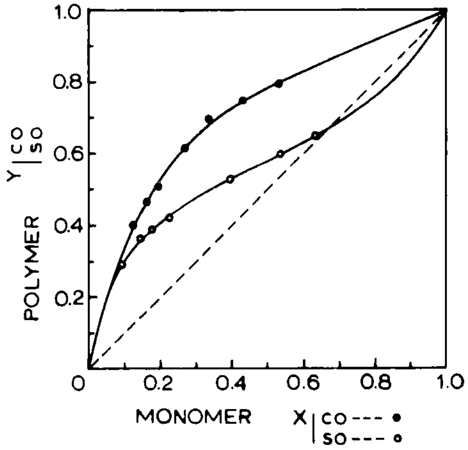


FIG. 3. Relationship between copolymer composition and comonomer charge; (○) styrene oxide, (●) cyclohexene oxide. Each with epichlorohydrin.

$r_2 > 1$) and a relatively small r_1 value (where $r_1 < 1$), produces the typical copolymerization curve with no inflection point. The ECH-SO system's copolymerization curve, which has an inflection point, is also typical for the range of values encountered, $r_1 < 1$ and $r_2 < 1$ but $r_1 > r_2$. (See also Fig. 4.)

The number-average molecular weights of the copolymers produced are not high. As the concentration of ECH is reduced in the respective copolymerization charges, the number-average molecular weight decreases. Because of the low molecular weights and the stoichiometry (initiator concentration, amount of the copolymer produced), it must be concluded that transfer takes place. Given the high concentrations of oxirane function in the copolymerizations, it is to be expected that oxonium ions would prevail in the mixture. Ready transfer from an oxonium ion, however, is not likely since such an entity is considered relatively

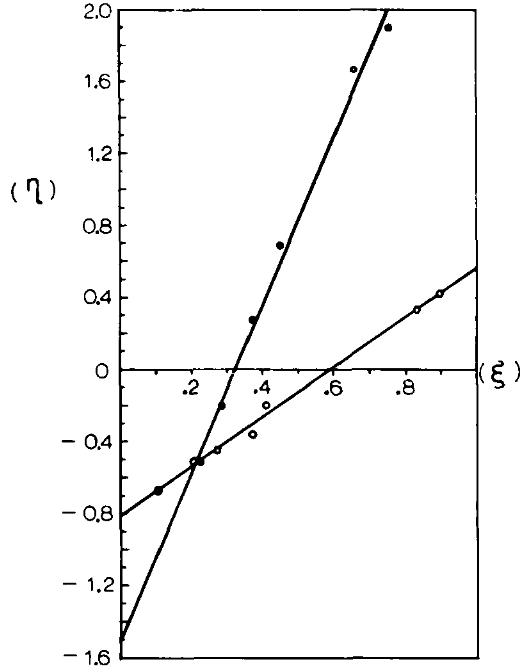
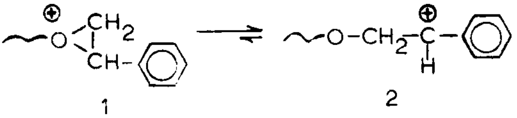


FIG. 4. Kelen-Tüdös plot to determine r_1 and r_2 values; (○) styrene oxide, (●) cyclohexene oxide. Each with epichlorohydrin.

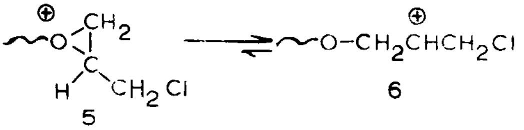
stable. Nevertheless, an equilibrium can be postulated between the respective chain and oxonium ions and an active carbocation.

Styrene oxide:



Cyclohexene oxide:

Epichlorohydrin:



Species 2, 4, and 6 would be expected to be sufficiently active to abstract hydride ions (H^-) from other species in the mixture, i.e., monomer. The experimental results suggest a relative order of activity for species 2, 4, and 6. Since the highest molecular weight is obtained when the polymerization charge has the highest ECH concentration, it must be that carbocation 6 does not readily enter into an abstraction process. The ECH/CO copolymerization charges produce oligomers with lower molecular weights than those found in the ECH/SO system. This suggests that species 4 is more reactive than species 2, which in turn is more reactive than species 6. Despite the fact that in all cases the equilibrium sits far to the left, species 2 and 4 exist at a finite concentration. When these carbocations abstract, the equilibrium is disturbed, reestablishes, and more transfer follows.

Both SO and CO homopolymers are soluble in diethyl ether while the homopolymer of ECH is not. The copolymerization product of ECH with CO was soluble in diethyl ether. However, the NMR of such a sample indicates that the copolymer contains ECH residues, indicating this must be a copolymer of ECH and CO. Our copolymerization products of ECH and SO were insoluble in diethyl ether. This copolymerization product before and after extraction with diethyl ether gave identical NMR spectra, which indicates that this product is also a real copolymer and not a mixture of ECH and SO homopolymers.

CONCLUSIONS

With the use of Ph_3CSbCl_6 as initiator, both epichlorohydrin (ECH) and 1,2-cyclohexene oxide (CO) can be copolymerized as can epichlorohydrin and styrene oxide (SO). The reactivity ratios indicate that in the ECH-SO case, ECH shows a strong tendency to form a copolymer containing short blocks of ECH residue while CO prefers cross propagation. In the copolymerization of ECH with SO, both monomers show a tendency to cross propagate, which gives a better alternating copolymer.

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