Terpolymerization of Cyclic Ethers with Cyclic Anhydride

H. L. Hsieh[a]

[a] Phillips Petroleum Co., Bartlesville, Oklahoma

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Phillips Petroleum Co.
Bartlesville, Oklahoma 74003

ABSTRACT

A unique solution polymerization and polymer family have been discovered in the ring-opening terpolymerization of three heterocyclic monomers initiated by organometallic compounds, particularly trialkylaluminum. The products have repeating ether-ester-ester linkages along the chain and are alternating terpolymers, ...ABCABCABC..., of three different monomers A, B, and C. Monomer A is a four- or five-membered cyclic oxide, such as tetrahydrofuran or oxocylobutane (oxetane). Monomer B is an epoxide, and Monomer C is a cyclic acid anhydride. Many epoxides and anhydrides participate in the polymerization which enables the preparation of alternating terpolymers containing various substituents and unsaturations at regular intervals along the chain. The alternating sequence can be near-perfect or less so depending on the initial monomer charge ratio. Evidence of the alternating structure was obtained by chemical and NMR analyses of polymer sampled at intermediate and final conversions, and by glass transition temperatures.

INTRODUCTION

Epoxides homopolymerize readily to form polyether but diabasic acid anhydrides do not. In the presence of certain catalysts, epoxides and cyclic acid anhydrides become bifunctional toward each other so that their interaction would give a linear polyester.
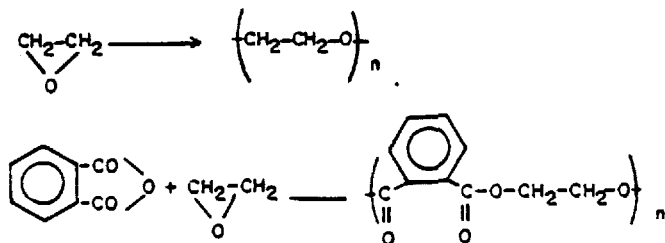
Tertiary amines and alkali metal salts such as lithium chloride and sodium acetate were reported [1-5] to catalyze the formation of essentially alternating copolymers. Other catalysts, such as $SbCl_5$, $SnCl_4$, $ZnCl_2$, and BF_3, can also catalyze copolymerization [6], but usually the copolymers contain some repeating epoxide units. In BF_3-catalyzed copolymerizations the copolymer composition depends on the charge ratio.

In recent years organometallic compounds have appeared on the scene as ring-opening polymerization catalysts [7]. Tsuruta et al. reported [8, 9] that alternating copolymers of epoxide and cyclic acid anhydride were formed with R_3Al and R_2Zn catalysts at relatively low temperatures ($30-80°C$) in toluene and dioxane. It was also reported [10] that tetrahydrofuran, a five-membered cyclic ether, does not polymerize with R_3Al alone but does polymerize in the presence of an epoxide. Furthermore it was shown [11] that copolymers of tetrahydrofuran and a cyclic acid anhydride can be prepared by the use of a three-component catalyst consisting of R_3Al or R_2Zn, water, and an epoxide. In view of these developments we explored the possibilities of modifying the polyester structure from alternating copolymerizations of epoxide and cyclic acid anhydride by inclusion of tetrahydrofuran.

EXPERIMENTAL

Toluene was dried by countercurrent scrubbing with nitrogen. Cyclic ethers and acid anhydrides were either distilled or recrystallized before use. Triisobutylaluminum was purchased from Texas Alkyls.

All polymerizations were done in beverage bottles. Anhydrides were weighed into the bottle first and then the bottle was flushed with nitrogen. Solvent was added and the bottle was flushed with nitrogen again before capping. Alkylene oxide was then added by hypodermic syringe. Initiator was generally added at room temperature.

Polymer solutions was acidified with excess, dilute hydrochloric acid just prior to recovery by coagulation in isopropyl alcohol or methanol. They were dried in a vacuum oven at 70°C for at least 16 hr.

RESULTS AND DISCUSSION

Ethylene oxide (EO) and epichlorohydrin (ECH) were mixed with phthalic anhydride (PA) in toluene with triisobutylaluminum [(i-Bu)$_3$Al] as catalyst (Table 1). The copolymers from ethylene oxide and phthalic anhydride in molar charge ratios of 1:1 and 2:1 were somewhat rich in ethylene oxide (this was confirmed by NMR work discussed later). With excess phthalic anhydride we feel, in view of the conversion, that an essentially alternating copolymer was formed although the analytical data did not differ greatly. Copolymers from epichlorohydrin and phthalic anhydride charged in mole ratios of 1:1 and 1:1.5 were essentially alternating. With excess epichlorohydrin the product must contain a certain amount of repeating epichlorohydrin units (ether-linkage). Both the conversion and analysis reflect this. IR analysis of all these copolymers clearly showed the presence of ester linkage.

When copolymerization of epichlorohydrin and phthalic anhydride was attempted in tetrahydrofuran, a completely different type of polymer was produced (Table 2). The alternating copolymer (a polyester) produced in toluene is a hard glassy solid, but the product formed in tetrahydrofuran was a soft, rubbery solid at room temperature. The total weight of polymer formed in tetrahydrofuran was not only significantly higher than in toluene, but greater than the epichlorohydrin (0.06 mole) and phthalic anhydride (0.06 mole) charged. The additional weight seemed to approach 0.06 mole of tetrahydrofuran. Elemental analysis also closely corresponded to 1:1:1 molar proportions of epichlorohydrin, phthalic anhydride, and tetrahydrofuran. Another experiment was run using tetrahydrophthalic anhydride (TCPA) in place of phthalic anhydride (Table 2). Tetrachlorophthalic anhydride is not very soluble in toluene, and the copolymer formed in toluene was rich in epichlorohydrin. Analysis of the polymer formed in tetrahydrofuran again suggested that the composition of the product contain equimolar amounts of the three monomers.

Before further work was done on the composition and structure

TABLE 1. Copolymerization of Epoxide and Phthalic Anhydride in Toluene

Epoxide			Phthalic anhydride		Polymer[a]	Analysis, %[b]			
Name	Mole	g	Mole	g	(g)	C	H	O	Cl
EO	0.12	5.5	0.12	18	16.9	60.4	4.5	36.7	-
EO	0.08	3.5	0.12	18	12.7	60.7	4.6	35.3	-
EO	0.24	11	0.12	18	16.0	59.7	4.9	36.9	-
ECH	0.12	11	0.12	18	26.4	54.5	4.0	27.7	14.7
ECH	0.08	7.5	0.12	18	19.5	54.7	4.2	26.2	14.7
ECH	0.24	22	0.12	18	33.6	53.8	4.4	25.8	16.4

[a] Polymerization in 200 ml toluene with 10 mmoles (i-Bu)$_3$Al at 70°C for 3 days.
[b] Calculated values:

	C	H	O	Cl
			%	
EO	54.6	9.0	36.4	0
PA	64.8	2.7	32.5	0
ECH	38.7	5.4	17.2	38.7
EO-PA (1:1)	62.5	4.2	33.3	0
ECH-PA (1:1)	55.8	3.7	26.5	14.7

TABLE 2. Polymerization of Epichlorohydrin and Phthalic Anhydride or Tetrachlorophthalic Anhydride in Toluene or Tetrahydrofuran[a]

Toluene (ml)	THF (ml)	Anhydride	Polymer (g)	Analysis (%)[b]			
				C	H	O	Cl
100	0	PA	12.5	54.6	4.0	28.1	14.4
0	100	PA	18.1	56.5	5.5	27.5	11.0
200	0	TCPA	7.5	35.5	2.9	18.5	42.1
0	200	TCPA	26.0	40.1	3.3	17.5	38.1

[a]ECH 0.06 mole (5.5 g), PA 0.06 mole (9 g), TCPA 0.06 mole (17 g), $(i\text{-}Bu)_3Al$ 4 mmoles for PA experiment and 6 mmoles for TCPA experiment, temperature 70°C, and 16 hr.
[b]Calculated values:

	%		
	C	H	O	Cl
ECH-PA (1:1)	55.8	3.7	26.5	14.7
ECH-PA-THF (1:1:1)	57.5	5.4	25.6	11.5
ECH-TCPA (1:1)	34.9	0.9	16.9	47.3
ECH-TCPA-THF (1:1)	40.0	2.9	17.7	39.4

of polymers prepared by copolymerizing epoxides, anhydrides, and tetrafuran, organometal compounds other than triisobutylaluminum were examined as catalysts. Water is the most commonly used co-catalyst with trialkylaluminum catalysts for ring-opening polymer-ization. In many cases it is absolutely necessary. In our ter-polymerization system, water in amounts greater than a R_3Al/H_2O mole ratio of 1/0.5 destroyed catalytic activity. Similar results were observed for MeOH as cocatalyst. Compounds such as Bu_3AlH, Et_2AlCl, and Et_2Zn were active. The usefulness of the latter catalyst, however, was limited to nonhalogenated monomers.

From polymerizations of the same two monomer combinations, namely epichlorohydrin/phthalic anhydride and epichlorohydrin/tetrachlorophthalic anhydride in toluene/tetrahydrofuran solutions of various compositions (Table 3), it was concluded that terpolymers of a 1:1:1 ratio can be prepared in toluene solvent but only if tetrahydro-furan is present in amounts significantly larger than required by stoichiometric terpolymerization.

TABLE 3. Formation of Terpolymers in Different Amounts of Tetrahydrofuran

Epoxide[a]	Anhydride[a]	Toluene/THF (ml)	Polymer (g)	Analysis (%)			
				C	H	O	Cl[b]
ECH	PA	100/0	13	53.4	4.0	28.8	15.0
ECH	PA	90/10	16	55.7	5.0	28.4	12.4
ECH	PA	60/40	18	56.1	5.3	27.7	11.6
ECH	PA	0/100	19[c]	56.2	5.4	27.9	11.4
ECH	TCPA	100/0	17	36.4	2.5	18.0	43.1
ECH	TCPA	90/10	25	39.8	3.3	18.7	38.3
ECH	TCPA	80/20	27[c]	–	–	–	–
ECH	TCPA	20/80	27	40.3	3.2	18.1	37.4
ECH	TCPA	0/100	27	40.1	3.3	17.5	38.1

[a]0.06 Mole each, $(i\text{-}Bu)_3Al$ 0.4 mmoles, temperature 70°C in 16 hr.
[b]Calculated values are 11.5 and 39.4 for ECH-PA-THF and ECH-TCPA-THF, respectively.
[c]Quantitative conversion for 1-1-1 terpolymer.

TABLE 4. Typical Examples of Epoxides and Anhydrides Used in Preparing Terpolymers with Tetrahydrofuran

Epoxides

Ethylene oxide	Glycidyl methacrylate
Propylene oxide	1,2-Epoxy-3-phenoxy-propane
Epichlorohydrin	Allylglycidyl ether
Styrene oxide	

Anhydrides

Phthalic anhydride	Succinic anhydride
Tetrachlorophthalic anhydride	Maleic anhydride
3-Nitrophthalic anhydride	Dichloromaleic anhydride
Trimellitic anhydride	Allylsuccinic anhydride
Endic anhydride	4-Cyclohexene dicarboxylic acid
Chloroendic anhydride	anhydride

Formation of terpolymers with this unique 1:1:1 composition is quite general with dibasic anhydrides and epoxides (Table 4). Some of the combinations which resulted only in low conversions of alternating copolymers in toluene could indeed form nearly quantitative conversions (based on 1:1:1 compositions) of terpolymers in the presence of a large excess of tetrahydrofuran. Unsaturated anhydrides and epoxides, such as maleic anhydride, allylsuccinic anhydride, and allylglycidyl ether, also form terpolymers with tetrahydrofuran. Use of pyromellitic dianhydride in more than 10 mole % of the total anhydride resulted in insoluble (cross-linked) polymers. Most of the terpolymers prepared had inherent viscosities in the range 0.2-0.3 in chloroform at 25°C.

Bis(chloromethyl)oxetane, a four-membered cyclic ether, was also a very active monomer for the formation of terpolymers containing epoxide and dibasic anhydride. To make polymers in toluene with a 1:1:1 composition, the minimum oxetane charge had to be at least double the required amount (Table 5).

Conversion and elemental analysis of these terpolymers had consistently indicated that the composition of these products corresponded to equimolar amounts of three monomers. To determine their distribution in the polymer chain, polymers sampled at intermediate conversion were examined (Table 6). Again elemental analyses demonstrated that the three monomers were present in the polymer chain in a 1:1:1 mole ratio throughout polymerization. These experimental results strongly suggested that these products are alternating terpolymers, i.e., $M_1 M_2 M_3 M_1 M_2 M_3 -$.

TABLE 5. Bis(chloromethyl)oxetane as Monomer[a]

| BCMO | | Alkylene oxide | | | Anhydride | | | Polymer | Found (calc) |
Mole	g	Type	Mole	g	Type[b]	Mole	g	(g)	% Cl
0.06	9.3	EO	0.06	2.7	-	-	-	Trace	-
0.06	9.3	-	-	-	PA	0.06	9.0	Trace	-
0.06	9.3	EO	0.06	2.7	PA	0.06	9.0	13	11.3 (20.5)
0.12	18.6	EO	0.06	2.7	PA	0.06	9.0	13	-
0.18	27.9	EO	0.06	2.7	PA	0.06	9.0	13	18.0 (20.5)
0.12	18.6	ECH	0.06	5.5	TCPA	0.06	17.0	31	45.7 (46.6)
0.12	18.6	ECH	0.06	5.5	NPA	0.06	11.6	11	22.2 (24.1)
0.12	18.6	ECH	0.06	5.5	CEA	0.06	22.2	30	50.7 (51.4)

[a]In 100 ml toluene with 4 mmoles $(i\text{-}Bu)_3Al$ at 70°C for 16 hr.
[b]PA = phthalic anhydride; TCPA = tetrachlorophthalic anhydride; NPA = 3-nitrophthalic anhydride; CEA = chloroendic anhydride.

More conclusive evidence for alternating structure came from NMR analysis. With ethylene oxide, phthalic anhydride, and tetrahydrofuran as monomers, the perfect alternating polymer should have the repeating unit
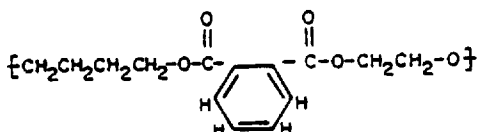
There are four types of protons and four protons of each type. Therefore the relative amounts of the three monomers present in the

TABLE 6. Compositions at Various Conversions of Epichlorohydrin/
Tetrachlorophthalic Anhydride/Tetrahydrofuran and Epichlorohydrin/
3-Nitrophthalic Anhydride (NPA)/Tetrahydrofuran Polymerizations

Conversion (%)[a]	Analysis (%)				
	C	H	O	Cl	N
ECH-TCPA-THF[b]					
39	41.3	3.5	18.1	38.0	-
65	40.6	3.5	18.9	39.0	-
82	40.2	3.3	18.6	41.2	-
97	40.1	3.3	17.5	38.1	-
Calc[a]	40.0	2.9	17.7	39.4	-
ECH-NPA-THF[c]					
30	49.2	4.4	33.5	9.7	3.8
54	49.3	4.5	33.4	9.7	3.8
88	49.7	4.9	32.8	10.2	3.6
Calc[a]	50.4	4.5	31.2	10.0	3.9

[a]Based on 1-1-1 ratio.
[b]ECH 0.06 mole, TCPA 0.06 mole, THF 200 ml, (i-Bu)$_3$Al 6 mmoles at 70°C.
[c]ECH 0.06 mole, NPA 0.06 mole, THF 100 ml, (i-Bu)$_3$Al 4 mmoles at 70°C.

TABLE 7

τ	Type of protons	Designation
2.1-2.7	Aromatic protons	A
5.3-5.9	$\overset{\displaystyle O}{\overset{\displaystyle \|}{-C}}-O-CH_2-$	B
6.1-6.7	$-O-\underline{CH_2}-$	C
8.0-8.7	$-CH_2-\underline{CH_2}-\underline{CH_2}-CH_2-$	D

TABLE 8. NMR Analysis of Polymer from Ethylene Oxide and Phthalic Anhydride Made in Tetrahydrofuran

Monomers charge					Mole ratio in polymer by NMR		
EO (mole)	PA (mole)	THF (ml)	Polymerization time (hr)[a]	Polymer (g)	EO	PA	THF
0.12	0.12	200	1.5	6.5	1.2	1.0	1.0
0.12	0.12	200	3.5	22	1.1	1.0	1.0
0.12	0.06	200	16	7.2	1.3	1.0	1.0
0.06	0.12	200	2	12	1.0	1.0	1.0
0.06	0.12	200	16	14	1.0	1.0	1.0

[a]At 70°C with 6 mmoles $(i\text{-}Bu)_3Al$.

TABLE 9. NMR Analysis of Polymer from Ethylene Oxide, Phthalic Anhydride, and Tetrahydrofuran Made in Toluene

Monomer charge (mole)[a]			Mole ratio in polymer by NMR		
EO	PA	THF	EO	PA	THF
0.06	0.06	0	1.5	1.0	0
0.06	0.06	0.06	1.2	1.0	0.45
0.06	0.06	0.12	1.1	1.0	0.60
0.06	0.06	0.24	1.0	1.0	0.73

[a]In 100 ml toluene with 4 mmoles $(i\text{-}Bu)_3Al$ at 70°C.

polymers can be calculated by examining the four regions in which the four kinds of proton resonance occur (Table 7).

The following ratios provide the desired information for terpolymer from ethylene oxide, phthalic anhydride, and tetrahydrofuran:

EO:PA:THF = B + C - D:A:D

The results are shown in Tables 8 and 9. Ethylene oxide has more tendency to homopolymerize than does epichlorohydrin in either the

formation of alternating copolymer with dibasic anhydride or alter-
nating terpolymer with anhydride and tetrahydrofuran or oxetane.
Nevertheless, when ethylene oxide was charged at less than the
equimolar ratio and tetrahydrofuran was in excess, near perfect
alternating terpolymer (an ether-ester-ester polymer) was prepared.
The T_g values and the sharp change in slope evident in the volume/
temperature relation are consistent with a repeating sequence
... $M_1 M_2 M_3$,... and inconsistent with block polymerization.

The mechanism of alternating terpolymerization is not clearly
understood at present. However, based on certain known and pub-
lished information, one can only speculate on the sequence of reactions
involved in such an orderly arrangement. The first step is complexing
of $R_3 Al$ with an anhydride which exhibits reactivity with epoxide to
form an alkylaluminum alkoxide [12]. The alkylaluminum alkoxide
thus formed reacts preferentially with tetrahydrofuran which is present
in large excess [10] and generates yet another alkoxide. This alkoxide
reacts preferentially with anhydride in the presence of epoxide, giving
a carboxylate [11, 12]. Alkylaluminum carboxylate then reacts
selectively with epoxide to reproduce alkylaluminum alkoxide [12].
Repetition of these reaction steps results in the formation of highly
alternating ether-ester-ester terpolymer. With lower levels of tetra-
hydrofuran, the alkylaluminum alkoxide formed from the epoxide is
more likely to react with anhydride, as in the case of the formation of
alternating polyester-copolymer, or occasionally, to add another unit
of epoxide (as in the case of ethylene oxide), introducing an ether
linkage.

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