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Alternating Copolymers from Alkyleneimines. I. Copolymers from Ethyleneimine and Dicarboxylic Anhydrides

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ABSTRACT

Ethyleneimine and dicarboxylic anhydrides were copolymerized to alternating copolymers which possess an ester-amide in the repeating unit. The structure of copolymer was identified by IR, NMR, and elemental analysis. On taking the structure of copolymer, the nucleophilic reactivity of ethyleneimine, and the electrophilic nature of dicarboxylic anhydride into consideration, a reaction mechanism was elucidated. It involves ring opening and a stepwise addition reaction in alternating manner, in that one monomer undergoes ring opening and chain propagation exclusively through the interaction with another monomer that is already present at the polymer chain end. The copolymers obtained from halogen containing dicarboxylic anhydrides are useful as fire-retarding additives for plastics and also as thermosetting resin precursor when anhydrides are partially replaced by maleic anhydride.

INTRODUCTION

Alkyleneimines polymerize readily but exclusively by acid catalysts and follows a stepwise addition polymerization [1]. Therefore, alkyleneimines are difficult to copolymerize with cyclic monomers which undergo polymerization by base catalysts and/or follow a chain propagation.

In this paper, we would like to report alternating polyesteramide obtained as copolymers between alkyleneimine and dicarboxylic anhydrides. The polymerization does not require any catalysts and follows a stepwise addition reaction by an alternating attack of one monomer on another which is already present at the polymer chain end. The alternating propagation in the absence of catalyst is attributed to the nucleophilic nature of alkyleneimine and the electrophilic reactivity of dicarboxylic anhydride.

EXPERIMENTAL

Monomers

Commercially available ethyleneimine was distilled, and the fraction distilling at 56-57° C was collected for use.

Dicarboxylic anhydrides such as phthalic anhydride, maleic anhydride, chlorendic anhydride (hexachloroendomethylenetetrahydrophthalic anhydride), succinic anhydride, 1,2-cyclohexane dicarboxylic anhydride, cis-cyclohexene-1,2-dicarboxylic anhydride, tetrabromophthalic anhydride, and tetrachlorophthalic anhydride were purified by either distillation or recrystallization.

Polymerization

Anhydrides were dissolved in dioxane. Insoluble anhydrides such as tetrachloro- or tetrabromophthalic anhydride were allowed to react in a suspension which became a clear viscous solution as the polymerization proceeded.

A solution of ethyleneimine and dioxane was then added to the anhydride-dioxane solution at such a rate as to keep the reaction temperature at 20-25° C, while cooling the reaction flask externally with water. When the addition was over, the mixture was stirred further for several hours at 25-30° C.

The reaction solution was poured in a nonsolvent for the resultant polymer, such as water or aliphatic hydrocarbon. The precipitated polymer was filtered, washed with solvent which dissolves monomer, and dried to constant weight in vacuo at 50° C.

Characterization

Polymers were analyzed for carbon, hydrogen, nitrogen, and halogen. The molecular weight was measured by the vapor pressure osmometric method. The glass transition temperature and the melting point were measured by differential thermal analysis.

The structure of polymer was analyzed by IR and NMR (60 MHz).

The results are shown in Table 1. The yield of polymer was almost quantitative, in most cases ranging from 93 to 100%.

RESULTS AND DISCUSSION

Structure of Polymers

As shown in Table 1, the yield of polymer is almost quantitative in most cases, and the elemental analyses indicate an equimolar composition of ethyleneimine and anhydride. The equimolar composition is confirmed from separate analyses of carbon/hydrogen, halogen, and nitrogen for the same polymer. For example, the carbon/hydrogen content analyzed for ethyleneimine-tetrachlorophthalic anhydride copolymer shows good agreement with that calculated for the equimolar composition. Similarly, both nitrogen and chlorine analyses show good agreement with the equimolar composition.

The copolymer of ethyleneimine-maleic anhydride was insoluble and infusible. As discussed in a separate paper, the unsaturation of maleic anhydride may also participate in the reaction in addition to the anhydride group, since maleic anhydride is an α,β-unsaturated dicarboxylic anhydride [2].

The IR spectra of ethyleneimine-phthalic anhydride copolymer indicated the presence of ester carbonyl at 1720 cm^{-1} and amide group at 1630 cm^{-1} along with several strong and broad absorptions at 1300-1000 cm^{-1} (C–O) and at 800-700 cm^{-1} (aromatics). It suggests an ester-amide linkage for the polymer structure.

The NMR spectrum of ethyleneimine-dicarboxylic anhydride copolymer is represented in Fig. 1, by that of ethyleneimine-phthalic anhydride copolymer. It shows two major peaks at δ 7.3-8.0 (A),

TABLE 1. Polyesteramides from Ethyleneimine and Dicarboxylic Anhydrides[a]

Dicarboxylic anhydride[b]	Analysis found (calcd)[c]				$\overline{M}_n$[d]	DTA analysis	
	C (%)	H (%)	X (%)	N (%)		T_g (°C)	Mp (°C)
Phthalic	62.0 (62.8)	4.9 (4.7)	–	7.5 (7.3)	3000	61	–
Chlorendic	33.5 (31.9)	2.0 (1.7)	47.0 (51.4)	3.1 (3.4)	2070	80	160
Maleic	48.8 (51.1)	6.1 (5.0)	–	10.6 (9.9)	–	Insoluble	–
Chlorendic-maleic[e]	36.5 (35.5)	2.9 (2.3)	39.8 (41.9)	4.4 (4.6)	2956	55	155-179
Succinic	48.2 (50.4)	6.7 (6.3)	–	10.3 (9.8)	–	–	–
1,2-Cyclohexane	59.2 (60.9)	7.7 (7.6)	–	6.3 (7.1)	1260	39	> 79[f]
cis-Cyclohexene-1,2	59.2 (61.5)	7.1 (6.7)	–	7.4 (7.2)	–	56	> 79[f]
Tetrabromophthalic	24.1 (23.7)	6.4 (9.9)	61.1 (63.1)	2.7 (2.8)	–	47	154
Tetrachlorophthalic	36.6 (36.5)	1.6 (1.5)	42.0 (43.1)	4.0 (4.3)	–	65	210

[a] Yields are almost quantitative, ranging from 93 to 100%.

[b] Ethyleneimine: dicarboxylic anhydride = 1 : 1 molar ratio.

[c] Calculated for 1:1 molar ratio of ethyleneimine and anhydride.

[d] By the vapor pressure osmometric method.

[e] Ethyleneimine:chlorendic anhydride:maleic anhydride = 1 : 0.6 : 0.4 molar ratio.

[f] Broad range.

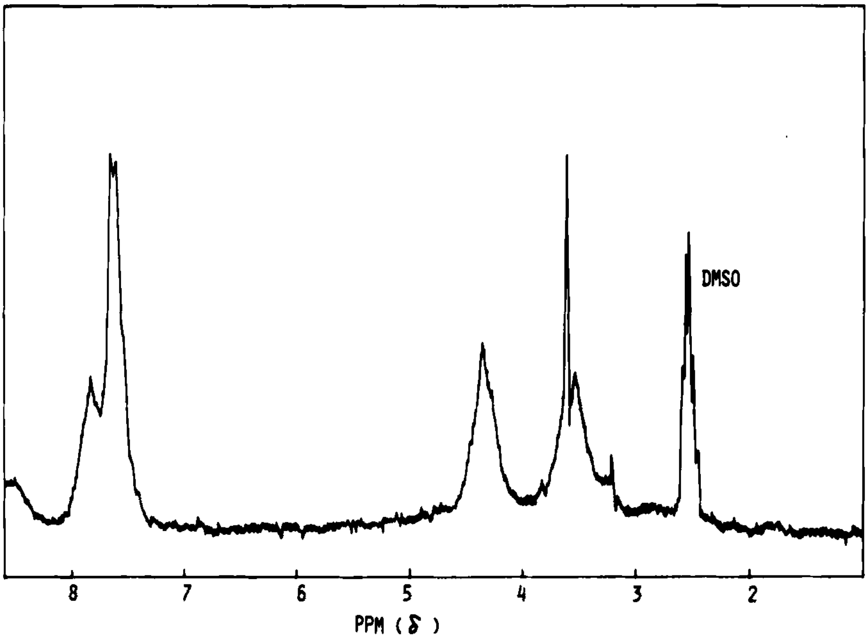
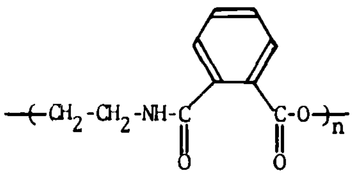


FIG. 1. NMR spectrum of ethyleneimine–phthalic anhydride copolymer in DMSO (60 MHz).

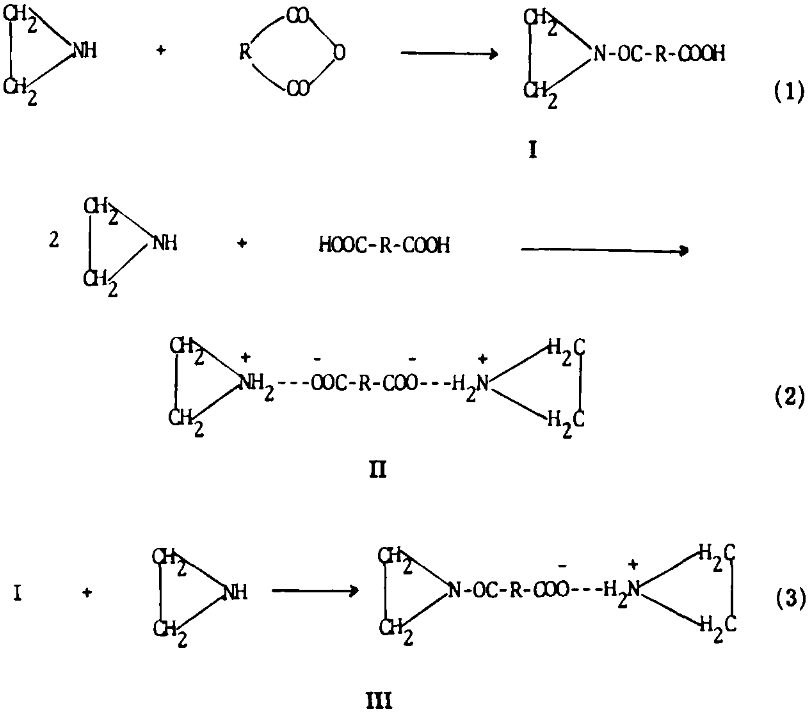
and at δ 4.7-3.2 (B) that can be assigned to the aromatic protons of phthalic anhydride and the methylene protons of ethyleneimine, respectively. The peak centered at δ 4.36 is due to the methylene protons of $-OCH_2-$, while peak centered at δ 3.6 could be assigned to the methylene protons of $-NCH_2-$ of ethyleneimine in the copolymer. From the integration value of peaks A and B, both ethyleneimine and phthalic anhydride units in the copolymer were calculated to be 50 mole %, indicating an alternating structure.

Thus, the results from elemental analysis and IR and NMR spectra best rationalize the alternating polyesteramide structure for the copolymer of ethyleneimine and phthalic anhydride, i.e., polyethylenephthalamate.



Reaction Mechanism

Since dicarboxylic anhydride might contain some free acid, the initiation step of copolymerization could involve either process (1) or (2).



In fact, the reactions (2) and (3) are part of chain propagation, and the salts II and III are known as intermediates in the ring-opening reaction of ethyleneimine by acid catalysts. Thus, the reactive salts II and III become free amines (IV) according to Eq. (4), a known reaction product between ethyleneimine and acid compound. The free amine now attacks the anhydride to form an ester-amide with a free carboxylic group which repeats the reaction (2) or (3) with ethyleneimine to form an ester-amide with a free amine group, i.e., the product IV. Thus, the propagation of polymer chain involves an alternating attack of one monomer on another which is already present in the polymer chain end as either acid or amine group. Apparently, such a propagation mechanism is entirely due to the nucleophilic or electrophilic nature of each monomer. The ester-amide (VI) becomes the repeating unit of the copolymer between ethyleneimine and dicarboxylic anhydride, i.e., an alternating polyesteramide

$$\text{II or III} \longrightarrow \sim\sim R\text{-}COO\text{-}CH_2\text{-}CH_2\text{-}NH_2 \qquad (4)$$

IV

(5)

V

$$\Longrightarrow \quad \sim\sim\sim(\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}OC\text{-}R\text{-}COO\text{-})_n\sim\sim\sim \qquad (6)$$

VI

The termination step should involve an ion association leading to a salt between amine and carboxylic groups of polymer chain, end since the relative number of either free amine or carboxylic group to that of monomers rapidly increases as the reaction proceeds. The salt formation would be one of the reasons for that copolymers obtained here are generally of low molecular weight. The salt VII formed between two polymers is assumed to be inactive at the reaction conditions employed in this work.

$$(VI)\sim\sim\sim COOH \quad + \quad H_2N\sim\sim\sim(VI)$$

$$\longrightarrow \quad (VI)\sim\sim\sim \overset{-}{COO}\text{---}H_2\overset{+}{N}\sim\sim\sim(VI) \qquad (7)$$

VII

APPLICATIONS

Although the molecular weight could be increased by refining the reaction and the process, several applications were investigated based on the low molecular weight nature of the reaction products.

Since there are a number of halogenated dicarboxylic anhydrides such as chlorendic anhydride, tetrabromophthalic anhydride, and tetrachlorophthalic anhydride, polyesteramides derived from these anhydrides are useful as fire-retarding additives for plastics.

As shown in Table 2, polyesteramides were compounded with ABS along with some other additives to give various halogen contents. They were then injection-molded to give bars for physical tests. Comparing samples B and C with sample A, the retention of physical properties of samples containing polyesteramide is remarkably high in spite of more than 20% of polyesteramide and 15% of the other additives that reduce the rubber content and generally the physical property of ABS as well to considerable extent. Particularly, the samples show a high retention of impact strength which is quite often the most sensitive physical property and decreases drastically in the presence of external additives.

On the other hand, the fire-retarding property of ABS is dramatically improved by introducing polyesteramide. Samples B and C were virtually nonburning, and thus more than nine out of ten samples passed the UL-94 test.

There is another positive aspect of polyesteramide as a fire-retarding additive. Most commercial fire-retarding additives tend to migrate out to the polymer surface, causing "blooming" during the molding process. This is due to the low molecular nature of conventional fire-retarding additives which are quite mobile within the polymer matrix, particularly at high temperatures as are used in molding. However, the blooming problem is resolved by using polyesteramide, the mobility of which is considerably limited owing to its high molecular weight.

Since dicarboxylic anhydride could be partially replaced by maleic anhydride without causing crosslinking, unsaturated polyesteramide could be readily obtained. The unsaturated polyesteramide is crosslinkable in the presence of unsaturated monomer and free-radical initiator, resulting in a thermosetting resin similar to the unsaturated thermosetting polyesters. The unsaturated polyesteramide derived from halogenated anhydride thus becomes a fire-retarding thermosetting resin. However, there is one limitation: the polyesteramide is not soluble in nonpolar vinyl monomers such as styrene which are generally used for the unsaturated polyesters. The insolubility is due to the amide group of polyesteramide. Instead of nonpolar vinyl

TABLE 2. Physical Properties of Fire-Retardant ABS from Polyesteramide[a]

	Sample A	Sample B	Sample C
ABS resin (parts)	100	100	100
FR additives (parts)			
Polyesteramide[b]	0	30.9	40.9
Sb_2O_3	0	10.3	10.3
Other additives (parts)[c]	2.5	16.2	16.2
Halogen content (%)	0	12.4 (Br)	12.6 (Cl)
Physical properties			
Tensile strength (psi)	6797	5410	5370
Flexural strength (psi)	11580	9950	9410
Izod impact strength (ft-lb/in. notch)	7.2	4.4	5.8
Heat deflection temperature (°C at 264 psi)	77	73	67
FR-property (UL-94)[d]	0/10	10/10	9/10

[a] ABS resin (19.8% polybutadiene, S/AN = 2.6) was compounded with fire retardant and the other additives, and injection-molded to give a bar of 1/2 in. width, 1/8 in. thickness, and 5 in. length. These bars were used for physical measurement.

[b] Sample B contains polyesteramide of tetrabromophthalic anhydride-ethyleneimine while sample C contains copolymer of chlorendic anhydride-ethyleneimine.

[c] Sample A contains 1 part 4,4'-butylidene-bis(6-tert-butyl-m-cresol), 1 part Mg stearate, and 0.5 part dilauryl thiodipropionate while samples B and C contain 9 parts TiO_2, 3 parts ZnO, 1.2 parts each of dibutyltin dilaurate, Mg stearate, and 4,4'-butylidene-bis(6-tert-butyl-m-cresol), and 0.6 part dilauryl thiodipropionate.

[d] Number of samples passing the test/number of samples tested.

monomers, however, some other polar monomer such as vinyl esters and acrylic monomers are useful for the unsaturated polyesteramide.

Thus, polyesteramide derived from chlorendic anhydride (0.8 mole), maleic anhydride (0.2 mole), and ethyleneimine (1 mole) was obtained in 100% yield. Analysis showed 35.3% carbon, 2.6% hydrogen, 43.2% chlorine, and 3.5% nitrogen; calculated values were 33.4% C, 2.9% H, 47.4% Cl, and 3.9% N, based on the alternating composition. It was dissolved in divinyl ether–butanediol and heated up in the presence of 1% benzoyl peroxide to give a clear, tough and cured material which was fire retardant.

The other conceivable application is to use polyesteramide as antielectrostatic additives for plastics and fibers, since the polymers contain highly polar acid and amine groups at the polymer chain end in addition to the ester and amide groups at the backbone.

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