Synthesis of Polyanhydride. I. Mixed Anhydride of Aromatic and Aliphatic Dibasic Acids*

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(Received February 4, 1959)

The polyanhydride of aromatic dibasic acid was first prepared by Bucher and Slade[1], who reported that the crystalline polymer of the melting point above 300°C was obtained by heating isophthalic acid or terephthalic acid with acetic anhydride. Aliphatic polyanhydride was synthesized in 1932 by Hill and Carothers[2] who have investigated the preparation of polyanhydride from sebacic acid. Although possessing fiber-forming properties, it was reported that the aliphatic polyanhydride melted at too low a point to be of practical interest and the polymer gradually disintegrated in the presence of moisture due to hydrolytic degradation. On account of these unfavorable properties, the study of polyanhydride has not been taken into consideration since then. In 1957, however, Conix[3] reported that aromatic polyanhydride prepared from di-(*p*-carboxyphenoxy)-α,ω-alkane has shown excellent film and fiber-forming properties. This might be ascribed to the hydrophobic nature of polymer molecules, caused by the accumulation of phenylene nuclei along the polymer chain to form a regular molecular structure very closely packed as observed in polyethylene terephthalate.

The present investigation has been undertaken in order to study the synthesis

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* Presented before the 4th Autumnal Meeting of the Chemical Society of Japan, held in Tokyo, November 23, 1958.

[1] J. E. Bucher and W. C. Slade, *J. Am. Chem. Soc.*, **32**, 1319 (1909).

[2] J. W. Hill and W. H. Carothers, ibid., **54**, 1569 (1932).

[3] A. Conix, *Makromol. Chem.*, **24**, (1) 76 (1957); *J. Polymer Sci.*, **29**, 343 (1958).

of mixed polyanhydrides of aromatic and aliphatic dibasic acids. As described herein, the mixed polyanhydrides of random structure were obtained when the calculated amount of aromatic and aliphatic dibasic acids had been mixed and treated with acetic anhydride which caused them to polymerize by heating in vacus. When suitable amounts of aromatic and aliphatic dibasic acids were used, it was possible to obtain mixed polyanhydrides of practical interest having their melting points in the range of 200 to 250°C. Using terephthalic acid as aromatic dibasic acid and adipic acid or sebacic acid as aliphatic dibasic acid, the mixed dibasic acids can be transformed into mixed anhydride with acetic anhydride. These mixed anhydrides polymerize by splitting off acetic anhydride. The diagram of composition versus melting point was obtained. From this the composition of mixed polyanhydride having its melting point in the range of 200°C to 250°C has been obtained for terephthalic acid-adipic acid, and terephthalic acid-sebacic acid copolymers.

Furthermore, the preparation of aromatic and aliphatic mixed polyanhydrides of regular structure have been investigated by the polycondensation reaction of diacid halide with dibasic acid in organic solvent pairs such as pyridine-benzene and pyridine-ether. The mixed polyanhydrides of regular structure having their melting points at 225°C (adipic acid) and 215°C (sebacic acid) have been synthesized, and the influence of chemical structure on the physical properties of these polymers was discussed[4].

Experimental and Results

Materials.—Commercially available sebacic acid and adipic acid were recrystallized from ethanol. The melting point was 133°C and 151∼153°C, respectively. The purified terephthalic acid was obtained by converting it into dimethyl ester, followed by vacuum distillation and alkaline hydrolysis. Thus, carefully purified aliphatic and aromatic dibasic acids were used as a starting material for each polymerization.

Mixed Polyanhydride of Random Structure.—The mixed polyanhydride of terephthalic acid and adipic acid was obtained by polycondensation reaction using the excess of acetic anhydride. The detailed procedure is described as follows.

A 13.3 g. (0.08 mol.) portion of terephthalic acid and 17.5 g. (0.12 mol.) of adipic acid were mixed together and 415 ml. of acetic anhydride (b. p. 130°C) were added to the mixture. The combined solution was refluxed on an oil bath at 150∼160°C for 8 hr. After the dibasic acids were completely dissolved into acetic anhydride, reflux was continued for an additional one hour and the excess of acetic anhydride was distilled off under water jet pump pressure to form mixed anhydride of low melting crystalline solid. The prepolymer thus formed was heated under dry nitrogen atmosphere in vacuo at 240°C for 1.5 hr. The resulting polyanhydride has its melting point at 235°C and possesses fiber-forming property. The intrinsic viscosity of polymer measured in 1,4-dioxane at 30°C was 0.130. However, it becomes brittle shortly after spinning due to its hydrolytic degradation by absorbing moisture. When purified terephthalic acid and adipic acid were used, it was possible to avoid coloration by impurities on heating.

The relationship between the melting point and the composition of terephalic acid and adipic acid was measured and its mole fraction was plotted against the melting point of copolymer as shown in Fig. 1. It gives the minimum melting point at 47∼48°C where the composition of copolymer is 93 mol. % of adipic acid. Polyanhydride of terephthalic acid itself has its melting point above 410°C. Two acids, e. g., terephthalic acid and aliphatic acid, furnish a series of copolymers in which the melting point and degree of crystallinity increase as the proportion of terephthalic acid is increased over 10 mol. %.

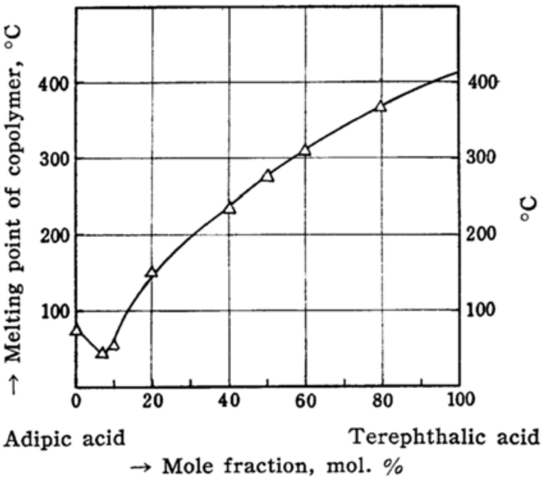

Fig. 1. Relation between composition and melting point of adipic acid-terephthalic acid anhydride copolymer.

The experimental results are summarized in Table 1. The infrared spectrum of the polymerization product has absorption bands of anhydride carbonyl group at 5.56 and 5.78 μ as illustrated in Fig. 2[5].

The polycondensation proceeds smoothly upon heating in vacuo to obtain a linear polymer and

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4) N. Yoda, *Makromol. Chem.* **32**, (1) 1 (1959).

5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 2nd. Ed., Methuen & Co., London (1958), p. 127—129.

TABLE I. COMPOSITION AND MELTING POINT OF TEREPHTHALIC ACID-ADIPIC ACID ANHYDRIDE COPOLYMERS

Expt. No.	Terephthalic acid mol. %	Adipic acid mol. %	m. p., °C	Properties	$[\eta]^{30^\circ C}_{1,4\text{-Dioxane}}$
1	0	100	75～ 77	Crystallizes readily	—
2	7	93	47～ 48	Crystallizes readily	—
3	10	90	53～ 55	Crystallizes readily	—
4	20	80	150～155	Crystallizes, fiber-forming	0.116
5	40	60	235	Crystallizes, fiber-forming	0.130
6	50	50	275	Crystalline solid	—
7	60	40	310	Crystalline solid	—
8	80	20	365	Crystalline solid	—

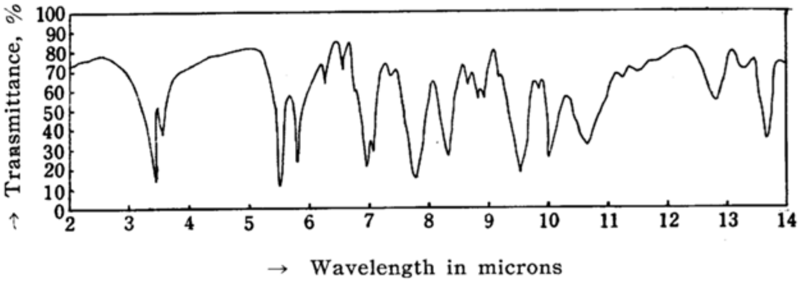


Fig. 2. The infrared spectrum of polyanhydride of adipic acid-terephthalic acid system (KBr).

the infrared data support the fact that the chains link with each other by anhydride groups and are terminated by acetyl groups derived from the reagent used in bringing about the anhydride formation.

The polymerization is started even by simple heating at 220～250°C at atmospheric pressure. A much faster reaction, leading to the formation of polyanhydride of higher molecular weights is observed, however, on heating the mixed anhydrides in vacuo under dry nitrogen atmosphere at elevated temperatures in order to facilitate the removal of acetic anhydride.

In the same manner, the mixed polyanhydride of terephthalic acid and sebacic acid was prepared by polycondensation of purified sebacic acid and terephthalic acid. The detailed procedure is illustrated below.

A 17 g. portion (0.10 mol.) of terephthalic acid and 40 g. (0.20 mol.) of sebacic acid were pulverized and 1000 ml. of acetic anhydride was added to the mixture. The solution was refluxed at 150～160°C for 8 hr. After distilling off the excess of acetic anhydride, a mixed anhydride of low melting crystalline solid was obtained. The prepolymer was heated under dry nitrogen atmosphere in vacuo at 230°C for 1.5 hr. to form polyanhydride having its melting poing at 220°C. This possesses a fiber-forming property and it is somewhat elastic. It becomes brittle shortly after spinning due to its hydrolytic degradation by absorbing moisture. The intrinsic viscosity of polymer measured in *p*-dioxane at 30°C immediately after spinning was 0.162.

The relationship between the melting point versus the composition of terephthalic acid and sebacic acid was obtained and its mole fraction was plotted against the melting point of copolymer as shown in Fig. 3. It was found that the minimum melting point was at 75°C where the composition of copolymer was 95.6 mol. % of sebacic acid and 4.4 mol. % of terephthalic acid. The experimental results are summarized in Table II. The infrared spectrum of copolymer has carbonyl absorption bands at 5.56 and 5.78 μ as shown in Fig. 4[5)].

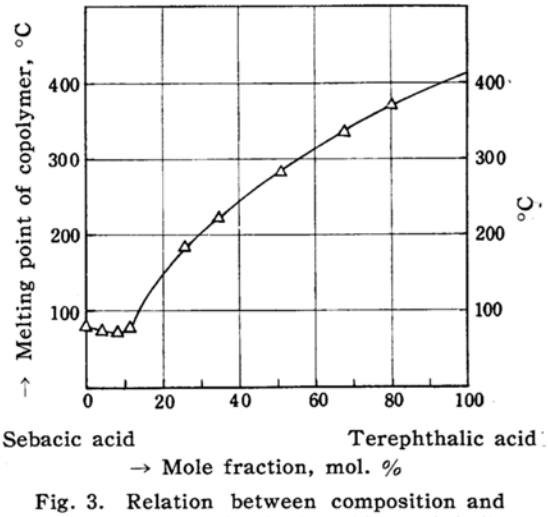


Fig. 3. Relation between composition and melting point of sebacic acid-terephthalic acid anhydride copolymer.

Infrared spectra indicate that polyanhydride before hydrolysis has two carbonyl absorption

TABLE II. COMPOSITION AND MELTING POINT OF TEREPHTHALIC ACID-SEBACIC ACID ANHYDRIDE COPOLYMERS

Expt. No.	Terephthalic acid mol. %	Sebacic acid mol. %	m. p., °C	Properties	$[\eta]^{30°C}_{1,4\text{-Dioxane}}$
1	0	100	79~80	Crystallizes readily	—
2	4.4	95.6	78	Crystallizes readily	—
3	8.5	91.5	75	Crystallizes readily	—
4	11.0	89.0	80	Crystallizes readily	—
5	25.9	74.1	185	Crystallizes, fiber-forming	0.081
6	34.4	65.6	220	Crystallizes, fiber-forming	0.162
7	51.1	48.9	280	Crystalline solid	—
8	67.7	32.3	335	Crystalline solid	—
9	80.7	19.3	370	Crystalline solid	—

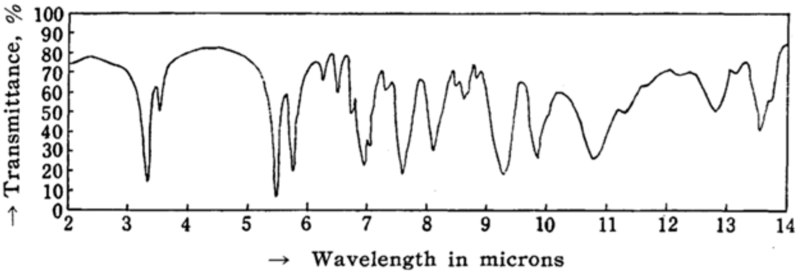


Fig. 4. The infrared spectrum of polyanhydride of sebacic acid-terephthalic acid system (KBr)

bands of the anhydride group at 5.56 and 5.78 μ. In addition to the carbonyl absorptions, the anhydride group also shows a strong band due to the C-O-C stretching vibration at 9.56 μ. When the polymer is exposed to moisture, the carbonyl absorption band at 5.86 to 5.95 μ appears. This indicates the existence of aliphatic and aromatic carboxylic acid carbonyl groups. The absorption bands at 3.71 and 3.95 μ are also observed. These can be taken as a strong evidence for the presence of dimeric carboxylic acid by taking account of bands existing in the carbonyl region.

When polyanhydrides of random structure are exposed to alkaline solution, it leads to the complete hydrolysis of anhydride to form aromatic and aliphatic dicarboxylic acids. An infrared spectrum shows neither anhydride carbonyl bands at 5.56 and 5.78 μ nor an ether band at 9.56 μ. On the contrary, the typical carboxylic acid bands appear at 3.71 and 3.95 μ of dimeric carboxylic acid bands and the strong carbonyl band at 5.86 μ[5].

The mixed anhydride of three components of dibasic acid such as the terephthalic acid, the adipic acid and the sebacic acid system was prepared by polycondensation reaction using the excess of acetic anhydride. The polymerization procedure is described as follows.

A 8.3 g. portion (0.05 mol.) of terephthalic acid, 7.3 g. of adipic acid (0.05 mol.) and 10.1 g. (0.05 mol.) of sebacic acid were thoroughly mixed in a mortar and refluxed with 550 ml. of acetic anhydride at 150~160°C for 8 hr. After all the acids were completely dissolved into acetic anhydride, the excess of acetic anhydride was distilled off under reduced pressure to form a mixed anhydride which was a low-melting crystalline solid. Then the prepolymer was heated under dry nitrogen atmosphere in vacuo at 250°C for 1.5 hr. to form a polyanhydride having a melting point at 245°C, which possesses a fiber-forming property.

Polymerization with acetyl chloride was also studied for dibasic acid anhydride of terephthalic acid and adipic acid or sebacic acid. In this case, the fiber-forming copolymer having a melting point at 210~230°C was also obtained with the mole fraction of 40 mol. % of terephthalic acid and 60 mol. % of adipic acid or sebacic acid.

Mixed Polyanhydride of Regular Structure.— Attempting to prepare the polyanhydride in which aromatic dibasic acid and aliphatic dibasic acid link with each other in a regularly bonded form, the polycondensation reaction of dibasic acid and dibasic acid chloride by dehydrochorination was studied in organic solvent pairs such as pyridine-ether, pyridine-benzene and dimethyl formamide-dimethyl aniline. Furthermore, the reaction of dibasic acid chloride with dimethyl ester of dibasic acid was investigated. In this case, terephthalic acid was again used for aromatic dibasic acid, and adipic acid or sebacic acid was chosen for aliphatic dibasic acid.

Preparation of Dibasic Acid Chloride.— Terephthalic acid chloride was prepared by the action of phosphorus pentachloride on terephthalic acid. After extraction with ether, it was dried over anhydrous sodium sulfate and the ether was evaporated off. The recrystallizations from ligroin after decolorization with activated charcoal gave colorless needles, m. p. 83.0°C (yield, 67%).

Adipic acid chloride was also obtained by refluxing adipic acid with the excess of thionyl chloride on a water bath for 4 hr. After evaporating off the excess of thionyl chloride, it gave adipic acid chloride which boiled at 112~115°C/10 mmHg (yield, 60%). Sebacic acid chloride was prepared in the same manner mentioned above with thionyl chloride to obtain a product boiling at 161°C/14 mmHg (yield, 45%). In order to avoid hydrolysis, the solvents used for the polymerization were carefully purified each time before use. Pyridine (C. P. grade) was refluxed with barium oxide and distilled, and the fraction at 115.5°C was taken. Benzene and ether were dried over metallic sodium and distilled immediately before use.

Polymerization in Pyridine-Ether Medium—A 4.5 g. portion (0.03 mol.) of terephthalic acid was dissolved into 120 ml. of pyridine and 5 g. (0.03 mol.) of adipic acid chloride dissolved into 100 ml. of ether were added dropwise into the reaction system with ice cooling under dry nitrogen atmosphere.

When acid chloride is added into pyridine, the pyridine complex is formed[6]. The reaction temperature was gradually raised to 25~30°C and stirring was continued for 4 hr. at this temperature. The resulting polymer was filtered, washed and dried to obtain polyanhydride having a melting point at 250°C. The existence of the anhydride group was confirmed by the infrared spectrum which showed acid anhydride absorption bands in a carbonyl region[5].

Polyanhydride of sebacic acid-terephthalic acid obtained under the same reaction condition has its melting point at 240°C, and the infrared spectrum has acid anhydride absorption bands in a carbonyl region[5].

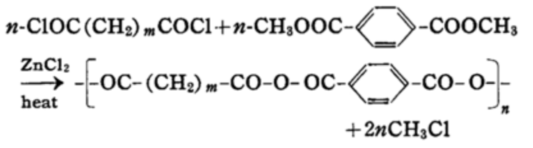
On the contrary, polyanhydride of terephthalic acid chloride and aliphatic acid forms a white crystalline solid, melting at 300°C with decomposition. The infrared spectrum shows acid anhydride and carboxylic acid absorption bands in a carbonyl region.

Polymerization in Pyridine-Benzene Medium.—When a pyridine-benzene solvent pair is used for the dehydrochlorination of terephthalic acid and aliphatic dibasic acid chloride, it was observed that the reaction proceeded more smoothly than in a pyridine-ether medium to form a white crystalline solid having its melting point at 225°C. The infrared spectrum shows carbonyl absorption band at 5.50 and 5.70 μ.

The reaction of sebacic acid chloride and terephthalic acid was also studied under the same reaction conditions, and white crystalline polymer melting at 215°C was obtained. The percent conversion of polyanhydrides in pyridine-benzene was found to be higher than that of polyanhydrides in pyridine-ether. The infrared spectrum indicates the existence of the acid anhydride group in a carbonyl region.

Polymerization of Dibasic Acid Chloride with Dibasic Acid Methyl Ester in the Presence of Zinc Chloride Catalyst.—As one of the processes to prepare polyanhydrides of regular structure, the polymerization reaction of dibasic acid chloride with dibasic acid methyl ester in the presence of zinc chloride was studied. The polyanhydrides of regular structure having their melting points at 203°C (adipic acid-terephthalic acid) and at 195°C (sebacic acid-terephthalic acid) were obtained.

Kyrides and Dvornikoff[7] reported the reaction of dialkyl phthalate and phthalyl chloride to give anhydride and the alkyl chloride. The improved method of the reaction of diacid chloride and diacid ester was employed in the presence of zinc chloride as a catalyst. The following reaction takes place for the polymerization in this case.



$m=4$ or 8

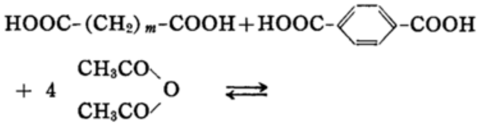
Although it is relatively stable against hydrolytic degradation, coloration of the polymer was observed when it was heated above 200°C.

In the same manner, polyanhydride obtained from sebacic acid chloride melts at 195°C and coloration occurs when it is heated above 200°C. It was found that the polymer thus obtained was relatively stable towards hydrolysis and it has a melting point with thermal decomposition. The polycondensation in dimethyl formamide medium was also studied and the polymers thus obtained failed to show good hydrolytic and thermal stability. It was found from the experimental results obtained above that the dehydrochlorination reaction of acid chloride and dibasic acid in pyridine-benzene medium gave the most satisfactory results.

Infrared Absorption Measurements.—The spectra were recorded with a Perkin-Elmer Model 21 spectrophotometer using an NaCl prism. Potassium bromide disks were used. The die and handpress were those supplied by the Shimadzu Co., Ltd.

Discussion

The polycondensation reaction of aromatic and aliphatic dibasic acids with acetic anhydride proceeds through the following equations; firstly, the dibasic acids are converted into mixed anhydrides with acetic anhydride as shown in Eq. 1.



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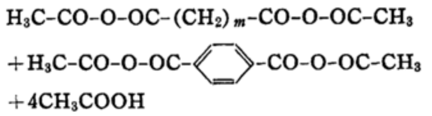
[6] E. C. Harning, "Organic Syntheses", Col. Vol. III, John Wiley & Sons, Inc., New York (1955), p. 28.

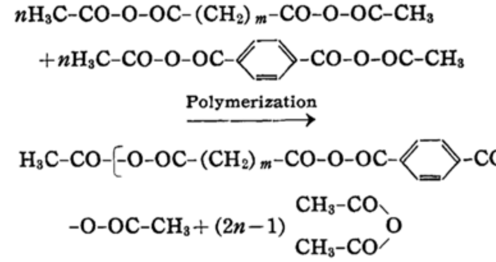
[7] L. P. Kyrides and M. N. Dvornikoff, *J. Am. Chem. Soc.*, 55, 4630 (1933).



(1)

$m=4$ or 8

Secondly, these mixed anhydrides thus formed, which bear terminal acetyl end-groups and are low-melting crystalline solids, polymerize upon heating by splitting off acetic anhydride to form polyanhydride with high molecular weights as indicated in the following Eq. 2.



(2)

$m=4$ or 8

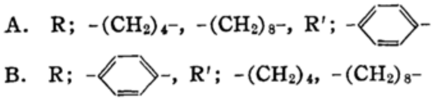
As to the mixed polyanhydride of random structure from aliphatic and aromatic dibasic acids, it was observed that the melting point and the degree of crystallinity increase with an increase in the proportion of aromatic dibasic acid. Presumably this can be explained by the fact that the introduction of aromatic nuclei into the polymer chain results in the formation of the polymer having rigid molecular structure due to the accumulation of phenylene nuclei along the polymer chain.

In the polymerization of polyanhydride of regular structure in pyridine-ether and pyridine-benzene media, the pyridine complexes of diacid chloride are first formed as shown in the following scheme:

$$\mathrm{ClOCRCOCl}+2\mathrm{C_5H_5N} \rightarrow \mathrm{R(COCl\cdot C_5H_5N)_2} \quad (3)$$

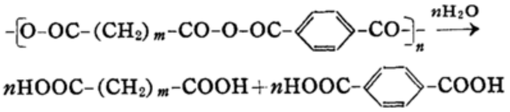
The pyridine complexes thus formed react with dibasic acid to obtain polyanhydride of regular structure as follows:

$$n\mathrm{R(COCl\cdot C_5H_5N)_2}+n\mathrm{R'(COOH)_2} \rightarrow$$
$$-\!\!\left[\mathrm{COR\text{-}CO\text{-}O\text{-}OC\text{-}R'\text{-}CO\text{-}O}\right]_n\!\!- + 2n\mathrm{C_5H_5N}+2n\mathrm{HCl} \quad (4)$$



There are possibilities that anhydride interchange reaction takes place during the dehydrochlorination process at an elevated temperature to be transformed into the polyanhydride of random structure. This can be avoided, however, when the polymerization is performed at room temperature or at slightly elevated temperature under atmospheric pressure.

It is reasonably presumed that acid anhydride groups in a less closely packed polymer chain (e. g., polyanhydride of random structure) are easily hydrolyzed in the presence of moisture[8], and the polyanhydride chain is disintegrated into low molecular weight dicarboxylic acid, as shown below:



(5)

The authors have further given their attention to the application of interfacial polycondensation[9] for the polymerization of polyanhydride, which involves a similar concept already mentioned in the case of polymerization in solvent pairs, using diacid chloride for one component in such organic solvent as chloroform or benzene, and sodium or potassium salt of dibasic acid or dimethyl ester of dibasic acid for another in aqueous alcohol phase at room temperature under nitrogen atmosphere[10]. Much room is left for the detailed study of polyanhydride synthesis in this field, and further investigation is necessary before it can be applied for general purposes.

Summary

Copolymerization reactions of mixed anhydrides of aliphatic and aromatic dibasic acids have been investigated. It has been shown that a polyanhydride of regular structure was obtained from diacid chlorides and dibasic acids in organic medium, and that polyanhydrides of random structure were obtained from the mixed aromatic and aliphatic dibasic acids. A polyanhydride having its melting point at 225°C was prepared for terephthalic acid and adipic acid copolymer of regularly linked structure and that having its melting point at 215°C for terephthalic acid and sebacic acid copolymer. It was found that the stability of copolymer towards hydrolytic and thermal degradations was greater for those with regularly

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[8] C. K. Ingold, "Structure and Mechanism In Organic Chemistry" Cornell Univ. Press, Ithaca, New York (1953), p. 754.

[9] E. L. Wittbecker and P. W. Morgan, Abstracts of the 134th Am. Chem. Soc. Meeting, Chicago, Illinois, (September, 1958), p. 8T—12T.

[10] N. Yoda, unpublished work.

linked structure than for a polyanhydride of random structure. The mixed polyanhydrides of random structure were prepared and the diagram of composition versus melting point was obtained. The mole fractions of the two acid components were found to be 35∼40 mol. % of terephthalic acid and 60∼65 mol. % of aliphatic dibasic acid for copolymers melting at 220 to 240°C. It has further been shown that aliphatic and aromatic dibasic acids furnish a series of copolymers in which the solubility decreases and the melting point and the degree of crystallinity increase as the proportion of aromatic dibasic acid is increased.

The authors wish to express their gratitude to Dr. K. Hoshino, the Director of the Research Department, and Dr. M. Watanabe for their interest in this research and the permission for its publication. Sincere thanks are also due to Professor Y. Ishii of Nagoya University for helpful discussion. The authors are indebted to Messrs. S. Tanaka and Y. Bamba for their cooperation in carrying out the experiments.

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