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Syntheses of Some Polymers Containing Cyclopropane Rings in the Main Chain

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SUMMARY:

Polyesters, polyamides, and polyurethanes containing cyclopropane rings in the main chains were prepared, using 1,2-cyclopropane dicarboxylic acid or 1,2-dimethylol-cyclopropane as one component. 1,2-Cyclopropane dicarboxylic acid and its homologs were synthesized according to the method of McCOY. The separation of the *cis* and *trans* isomers of these acids was performed by treatment with thionyl chloride, where the *trans* isomers were converted into acid chlorides, while the *cis* isomers into acid anhydrides. 1,2-Dimethylol-cyclopropane was prepared by the reduction of 1,2-cyclopropane dicarboxylic chloride with $LiAlH_4$.

The polymerization was carried out by the interfacial technique, ~~the~~ solution polycondensation, or the ester interchange method. Some polymers and their films showed good technological properties.

ZUSAMMENFASSUNG:

Polyester, Polyamide und Polyurethane, welche Cyclopropanringe in der Hauptkette enthalten, wurden unter Verwendung von 1,2-Cyclopropan-dicarbonsäure oder 1,2-Dimethylol-cyclopropan als eine Ausgangskomponente dargestellt.

Die 1,2-Cyclopropan-dicarbonsäure und deren Homologe wurden nach der Methode von McCOY hergestellt. Zur Trennung der dabei entstandenen cis- und trans-Isomeren wurde das Gemisch mit Thionylchlorid behandelt, dabei das trans-Isomere in das Säurechlorid, das cis-Isomere in das Dicarbonsäureanhydrid umgewandelt. Diese zwei Verbindungen konnten leicht durch fraktionierte Destillation getrennt werden. Das 1,2-Dimethylol-cyclopropan wurde durch die Reduktion von 1,2-Cyclopropan-dicarbonsäurechlorid mit $LiAlH_4$ erhalten.

Es wurden die Grenzflächenpolykondensation, die Polykondensation in Lösung und die Esteraustausch-Reaktion angewendet.

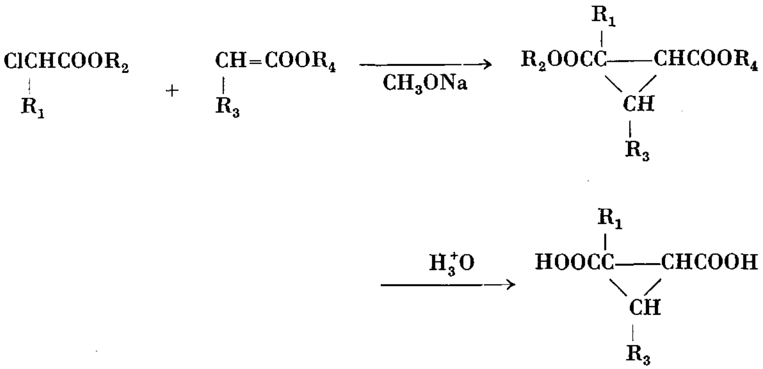
Einige erhaltene Polymere zeigten ausgezeichnete Filmeigenschaften.

1. *Introduction*

The syntheses of aliphatic polyesters, polyamides, and polyurethanes have long been studied by a great number of researchers and there are many literatures in this field. In these polymers, if the length of the sequence of methylene group in the main chain is short, good polymer properties can not be expected. However, the properties of polymers having cycloaliphatic rings in the main chain are generally better than those with straight aliphatic chain. In this sense, the syntheses of a series of polymers containing the smallest aliphatic ring, *i.e.*, cyclopropane ring in the main chain seems interesting. In this paper polyesters, polyamides, and polyurethanes were synthesized using 1,2-cyclopropane dicarboxylic acids or 1,2-dimethylol-cyclopropane as a monomer component.

a) *Syntheses of Dicarboxylic Acids and of 1,2-Dimethylol-cyclopropane*

1,2-Cyclopropane dicarboxylic acid and its homologs were synthesized according to the method of McCoy[1] as described below.



(1)

Table 1. Yields and physical data of the prepared dicarboxylic acids I

	Ester[a]		Acid[a]
	Yield (%)	b.p. (°C./mm.Hg)	m.p. (°C.)
$R_1 = H$; $R_2 = C_2H_5$; $R_3 = H$; $R_4 = CH_3$	42.5	90–100/10	116–120
$R_1 = CH_3$; $R_2 = CH_3$; $R_3 = H$; $R_4 = CH_3$	70	120–125/40	118–125
$R_1 = H$; $R_2 = C_2H_5$; $R_3 = CH_3$; $R_4 = C_2H_5$	28	92–96/5	–

[a] Mixtures of steric isomers.

Some methods of the separation of *cis* and *trans* isomers of 1,2-cyclopropane dicarboxylic acid have been reported[1,2].

Recrystallization method is one of them, in which the *cis* isomer is recrystallized from nitromethane and the *trans* isomer from water. However, it was confirmed that the separation by this method is not so sharp.

Another method is to convert the *cis* isomer into the *trans* isomer by heating with potassium hydroxide or sulfuric acid. For example, with potassium hydroxide as catalyst the yield of the *trans* isomer was 80 %. This method is suitable to obtain the *trans* isomer, which was proved to be superior as the component of polymer to the *cis* isomer. But, in the case of methyl substituted 1,2-cyclopropane dicarboxylic acids this method is not effective. We devised a method which was more effective for the separation of the *cis* and *trans* isomers of 1,2-cyclopropane dicarboxylic acid and its homologs.

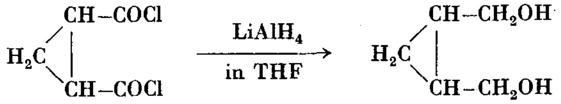
In our method, the mixture of the *cis* and *trans* isomers was treated with thionyl chloride, where the *cis* acid was converted into the acid anhydride and the *trans* one into the acid chloride. The ratios of the yields of the two isomers, thus found, are given in Table 2. In an independent experiment, we confirmed that under the conditions no change between the two isomers occurred. Therefore, the ratio of the yield may be taken to show the actual ratio in the reaction product.

Table 2. Ratios of the yields of the isomeric cyclopropane dicarboxylic acids

	Ratio of yield (%)	b.p. (°C./mm. Hg)	m.p. (°C.)	
1,2-Cyclopropane dicarboxylic	*Trans* 40	82–84/18		C[a]
acid	*Cis* 60	135–135.5/15	(58–60)	A[b]
1-Methyl 1,2-cyclopropane	*Trans* 20	101–105/28		C
dicarboxylic acid	*Cis* 80	140–145/28		A
3-Methyl 1,2-cyclopropane	*Trans* 50	68/8		C
dicarboxylic acid	*Cis* 50	–		A

[a] C; Acid chloride. [b] A; Acid anhydride.

1,2-Dimethylol-cyclopropane was obtained from 1,2-cyclopropane dicarboxylic chloride by reduction using lithium aluminum tetrahydride.



(2)

The reduction by lithium aluminum tetrahydride has been generally carried out using ethyl ether as solvent and the reduction of 1,2-cyclopropane dicarboxylic acid dimethyl ester by this method has been reported by BLOMQUIST[3]. The reported yield of corresponding glycol was 50 %. However, for the reduction of 1,2-cyclopropane dicarboxylic chloride tetrahydrofuran (THF) was found to be more suitable as the reaction solvent than ethyl ether, *i.e.*, the yield of the glycol was 85 % in THF and 40 % in ethyl ether.

b) *Syntheses of Polymers by Interfacial Polycondensation Method*

Polyamides

The interfacial polycondensation method developed by a research group of Du Pont Co. is the most useful for the synthesis of the polymer having high melting point and low solubility. Polyamides have been generally obtained easily by this method. We used three *trans* acids and one *cis* acid as the acid component and hexamethylene diamine, piperazine and others as amine component. Benzene was employed as organic solvent and sodium lauryl sulfate as emulsifier. The polymerization was performed by agitating the two components at high speed. The results are shown in Table 3.

Table 3. Preparation of polyamides by interfacial polycondensation

Acid chloride[a]	Diamine	Yield (%)	m.p. (°C.)	$[\eta]$[b] (g./100 ml.)
Trans C	Ethylene diamine	53	~350	0.43[c]
Trans C	Propylene diamine	10	~310	0.85[c]
Trans C	Hexamethylene diamine	35	~300	1.30
Trans C	Piperazine	58	~330	0.55
Cis C	Hexamethylene diamine	30	~180	0.37
Trans 1 MC	Hexamethylene diamine	40	~115	0.19
Trans 1 MC	Piperazine	8	~130	0.30
Trans 3 MC	Hexamethylene diamine	71	~270	0.27
Trans 3 MC	Piperazine	67	~280	1.38
Trans C + 3MC	Hexamethylene diamine	47	~240	0.55
Trans C + 3MC	Piperazine	70	~265	0.90

[a] C: 1,2-Cyclopropane dicarboxylic chloride. 1 MC: 1-Methyl-substituted C. 3 MC: 3-Methyl-substituted C.

[b] Measured in *m*-cresol, unless otherwise mentioned.

[c] Measured in 98% formic acid.

The polyamides obtained from *trans* acids, particularly from that having no methyl group showed low solubility and high melting point. The polyamides prepared from 3-methyl substituted *trans* acid were tough and stiff and gave good film.

On the other hand the polyamides from 1-methyl-substituted *trans* acid had low melting point and low intrinsic viscosity. These polymers were difficulty soluble in *m*-cresol and in 98% formic acid and insoluble in other common organic solvents. From *cis* acid the polyamides could not be obtained except only one case and even in that case the property of the polymer was not excellent.

Polyester

The yields of polyesters were generally higher than those of polyamides, and the polymer could be obtained even from *cis* acid. However, the polyesters were generally brittle. The dihydroxy compounds employed were bisphenol A, resorcinol and hydroquinone. The results are shown in Table 4.

Table 4. Preparation of polyesters by interfacial polycondensation

Acid chloride	Dihydroxy compound	Yield (%)	m.p. (°C.)	[η][a] (g./100 ml.)
Trans C	Bisphenol A[b]	90	~180	0.18
Trans C	Resorcinol	80	~105	0.13
Trans C	Hydroquinone	–	~260	–
Cis C	Bisphenol A	73	~120	0.08
Cis C	Resorcinol	68	~65	0.05
Trans 1 MC	Bisphenol A	63	~90	0.06
Trans 3 MC	Bisphenol A	61	~130	0.12

[a] Measured in dioxane.
[b] Bisphenol A = $HO(p)\text{–}C_6H_4\text{–}C(CH_3)_2\text{–}C_6H_4\text{–}(p)OH$.

Table 5. Preparation of polyesters by solution polycondensation

Acid chloride	Dihydroxy compound	Yield (%)	m.p. (°C.)	[η] (g./100 ml.)
Trans C	Bisphenol A	85	~145	0.15[a]
Trans C	Resorcinol	65	~105	0.11[a]
Trans C	Hydroquinone	–	~280	–
Cis C	Bisphenol A	77	~130	0.08[a]
Cis C	Hydroquinone	75	~160	0.03[b]
Adipyl chloride	*Trans* M[e]	–	Oil	–
Isophthaloyl chloride	*Trans* M[e]	–	~100	0.04[c]
Trans C	*Trans* M[e]	–	Oil	–
D.M.T.[d]	*Trans* M[e]	80	~130	0.25[c]
D.M.T.[d]	*Cis* M	50	~130	0.18[c]

[a] Measured in Dioxane. [b] In *m*-Cresol. [c] In Dimethylformamide.
[d] Dimethyl terephthalate. [e] 1,2-Dimethylol-cyclopropane.

c) *Syntheses of Polyesters by Solution Polycondensation and Ester Interchange Method*

The polyester can be also prepared by heating of the two components, such as dihydroxy compound and acyl chloride, in suitable solvent such as nitrobenzene. This method is applicable to the synthesis of polyester containing aliphatic alcohol component. However, the properties of polyesters obtained by this method were generally not excellent. The results are shown in Table 5. On the other hand, from an ester of aromatic dicarboxylic acid, the polyester can be obtained by the method of ester interchange. Using this technique, polyester was prepared from dimethyl terephthalate and 1,2-dimethylol-cyclopropane. The results are also shown in Table 5.

d) *Polyurethanes*

The polyurethanes were synthesized by two different methods. One is usual, that is, heating of equimolecular mixture of two components, such as, diisocyanate and 1,2-dimethylol-cyclopropane in a suitable solvent. We used toluylene diisocyanate, 4,4′-diphenylmethane diisocyanate, and hexamethylene diisocyanate as the diisocyanate component. The polymer thus prepared, especially that from 4,4′-diphenylmethane diisocyanate, showed good properties and gave good film.

The other is a method to employ the bis-chloroformate of 1,2-dimethylol-cyclopropane as an intermediate. The polyurethane can be obtained from the bis-chloroformate and appropriate diamine by interfacial polycondensation method. However, good polyurethanes could not be obtained by this method probably because of the impurity in the bis-chloroformate whose purification by distillation is difficult. The results are shown in Table 6.

Table 6. Preparation of polyurethanes

Diisocyanate or diamine	Dihydroxy compound	Yield (%)	m.p. (°C.)	$[\eta]$[a] (g./100 ml.)
D.M.I.[b]	*Trans* M	100	$\sim$290	1.23
D.M.I.[b]	*Cis* M	100	$\sim$230	0.98
Toluylene diisocyanate	*Trans* M	100	$\sim$200	0.35
Toluylene diisocyanate	*Cis* M	100	$\sim$170	0.34
Hexamethylene diisocyanate	*Trans* M	100	$\sim$165	0.35
Hexamethylene diisocyanate	*Cis* M	100	$\sim$120	0.25
Hexamethylene diamine	*Trans* M[c]	—	$\sim$130	0.16
Hexamethylene diamine	*Cis* M[c]	—	$\sim$90	0.06
Piperazine	*Trans* M[c]	—	$\sim$100	0.05
Piperazine	*Cis* M[c]	—	$\sim$70	0.04

[a] Measured in N,N-Dimethyl formamide.

[b] 4,4′-Diphenylmethane diisocyanate. [c] *Via* bis-chloroformate.

2. *Experimental*

a) *Reduction of 1,2-Cyclopropane Dicarboxylic Chloride by $LiAlH_4$*

A solution of 24 g. (0.143 mole) of 1,2-cyclopropane dicarboxylic chloride in 100 ml. of THF was added under stirring to a suspension of 10 g. (0.263 mole) of $LiAlH_4$ in anhydrous THF during 2 hrs. at 50 °C. After the mixture was stirred at 50 °C. for additional 1 hr., 30 ml. of water and then 300 ml. of 10 % H_2SO_4 were added to decompose the excess $LiAlH_4$. The THF layer was salted out, dried by magnesium sulfate and distilled. The *trans* and *cis* 1,2-dimethylol-cyclopropane was distilled at 93 °C./2 mm. Hg, the yield being 12.5 g. (85 %).

b) *Interfacial Polycondensation*

Polyamide

Under vigorous stirring an ice-cooled solution of 5.3 g. (0.032 mole) of *trans* 1,2-cyclopropane dicarboxylic chloride in 200 ml. of benzene was added dropwise to a solution of 3.7 g. (0.032 mole) of hexamethylene diamine, 7.0 g. (0.065 mole) of sodium carbonate and 0.7 g. of sodium sulfate in 120 ml. of water. After addition, the mixture was stirred for additional ten mins. and then the white product was collected on a mortar, filtered, washed, and dried. The polyamide was purified by reprecipitation using 98 % formic acid as solvent and water as precipitant.

Polyester

The reaction procedure was analogous to that of polyamide except that chloroform was used as organic solvent and the solution of acid chloride was added to aqueous solution of the dihydroxy component. After reaction was complete, the chloroform layer was separated, washed with water several times and the polyester was obtained by evaporating chloroform under reduced pressure. The polyester was purified by reprecipitation using acetone as solvent and water as precipitant.

c) *Synthesis of Polyester by Solution Polycondensation*

A solution containing 4.607 g. (0.04184 mole) of recrystallized hydroquinone and 6.983 g. (0.04184 mole) of freshly distilled *trans* 1,2-cyclopropane dicarboxylic chloride in 25 ml. of purified nitrobenzene was heated gradually under nitrogen atmosphere. At 110 °C. the evolution of hydrogen chloride was observed. The solution became viscous and some white solid began to precipitate when the solution was heated at 150 °C. for 1.5 hrs. and at 160 °C. for 2.5 hrs. After heating at 170 °C. for 4 hrs., the evolution of hydrogen chloride ceased. The polyester was obtained by removing of nitrobenzene under reduced pressure.

d) *Polyester by Ester Interchange*

The procedure was analogous to that of synthesis of polyethylene terephthalate. A mixture of antimony trioxide and calcium acetate was used as catalyst, and the reaction was carried out at 190 °C. for 1 hr., 285 °C. for 0.5 hr. at 10 mm. Hg and 285 °C. for 5 hrs. at 2 mm. Hg. The polyester was purified by reprecipitation using dioxane as solvent and methanol as precipitant.

e) *Synthesis of Polyurethane*

α) Under nitrogen atmosphere a solution of 3.48 g. (0.02 mole) of toluylene diisocyanate in 20 ml. of anisole was added with stirring to a boiling solution of 2.04 g. (0.02 mole) of purified 1,2-dimethylol-cyclopropane in 20 ml. of anisole. After refluxing and stirring for 4 hrs. a solution of 0.01 g. of the diisocyanate in 5 ml. of anisole was added further, and the mixture was refluxed for additional 2 hrs. The polyurethane prepared was treated with boiling ethanol, dried, and purified by reprecipitation using N,N-dimethylformamide as solvent and methanol as precipitant.

β) The bis-chloroformate of 1,2-dimethylol-cyclopropane was obtained by the reaction of 1,2-dimethylol-cyclopropane with excess of phosgen under ice cooling. The bis-chloroformate could not be purified by distillation and the crude bis-chloroformate was used in interfacial polycondensation.

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