[CONTRIBUTION FROM THE POLYMER RESEARCH LABORATORY, THE DOW CHEMICAL CO.]

Thermally Stable Hydrocarbon Polymers: Polyterephthalylidenes

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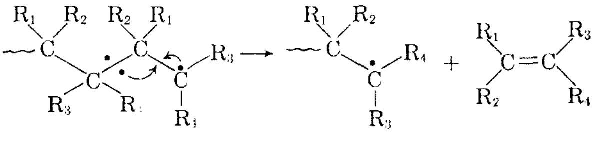
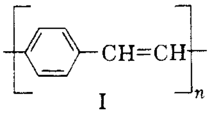
Polymers containing terephthalylidene repeating units were prepared by condensation polymerization employing the Knoevenagel reaction. Thermal stabilities of the polymers were interpreted on the basis of weight loss data and the change in the infrared spectra on pyrolysis. Thermal degradation at 550° resulted in a weight loss of less than 30% and the formation of a stable polymeric residue.

The current approach to the preparation of thermally stable plastics is to synthesize polymers with repeating units analogous in structure to compounds known or even thought to be thermally stable.[1] This approach necessitates the use of reactions which have not been sufficiently characterized to be satisfactorily applied to the formation of high molecular weight polymers. The main objective of this analogy approach, however, is to carry out the polymerization only to the point at which the polymeric products are nonvolatile and suitable for thermal degradation studies without attempting to achieve the degree of polymerization necessary for the realization of adequate stress-strain properties.

With the exception of polytetrafluoroethylene (Teflon), all linear polymers which have backbones consisting of only carbon-carbon bonds and which are prepared by addition polymerization of olefinic monomers are thermally unstable far below the present goal of 500°.[2] This instability is due to the thermodynamic reversibility of addition polymerization.[3] Kinetically, this instability is probably facilitated by the close energy couple characteristic of the elimination of a monomer unit from the radical end of a pyrolyzing polymer chain.[4] That is, the endothermic cleavage of the sigma bond in the chain is probably facilitated by the exothermic coupling of the two unpaired electrons remaining to form the pi bond in the monomer eliminated, as follows:



Condensation polymers cannot regenerate monomers on thermal degradation and, therefore, a close energy couple rarely exists. Accepting this characteristic and considering bond strengths, it should be possible to prepare by condensation polymerization a polymer with an all carbon-carbon backbone which would be kinetically stable above 500°. Several nonvinyl, hydrocarbon polymers have been studied from this point of view including polyphenylene,[5-7] poly-*p*-xylene,[8-11] phenol-formaldehyde polymers,[12] polybenzyl[13-15] and a polymeric Diels-Alder adduct.[16] These polymers were reported to be thermally stable up to temperatures ranging from a low of approximately 350° for polybenzyl to a high of 550° for polyphenylene. In the present study, condensation polymerizations employing the Knoevenagel reaction were applied to the preparation of polyterephthalylidene, I, and polycyanoterephthalylidene, II.



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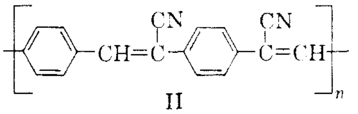

II

These polymers were of interest because pure compounds of this basic structure prepared by unequivocal synthetic routes were reported to be stable above 350°.[17,18] Attempts were made to prepare

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[1] C. S. Marvel and J. H. Rassweiler, *J. Am. Chem. Soc.*, **80**, 1197 (1958).

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[4] H. E. Remick, *Electronic Interpretations of Organic Chemistry*, John Wiley & Sons, New York, 1950, p. 522.

(5) G. A. Edwards and G. Goldfinger, *J. Polymer Sci.*, **16**, 589 (1955).

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(12) G. E. Dodson, *Research and Engineering*, No. **1**, 22 (January 1957).

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(16) W. J. Bailey, P. B. Rept. 121360, "Elastomer Research and Development, Vol. I," U. S. Dept. of Commerce, Office of Technical Services, 1956, p. 37.

(17) J. Schmitt, J. Boitard, M. Suqnet, and P. Comoy, *Compt. Rend.*, **242**, 649 (1956).

(18) G. Drefahl and G. Plötner, *Chem. Ber.*, **91**, 1274 (1958).

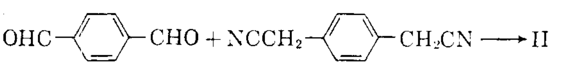
TABLE I

SOLUTION POLYMERIZATION OF TEREPHTHALALDEHYDE AND BENZENE-1,4-DIACETONITRILE

Polymerization	Catalyst	Reaction Temp.	Color of Polymer	Empirical Formula[a]	Aldehyde Content[b]	Decomposition Temp. In Air
A	Sodium methoxide	25-78	Orange	$C_{20}H_{13}N_2O_{2.4}$	5-10%[c]	440-480
B	Piperidine	25-78	Yellow	$C_{18}H_{11}N_2O_{1.1}$	[d]	—
C	Sodium ethoxide	5	Orange	$C_{18}H_{11}N_2O$	5-10%[e]	500-510
D[f]	—	—	Rust	$C_{20.5}H_{13}N_2O_{0.5}$[g]	—	480

[a] Theoretical formula for linear polymer: $C_{18}H_{10}N_2$. [b] By infrared analysis. [c] Ratio of C=C—CN to C—C—CN approximately 30 to 1 by infrared analysis; approximately 25% crystalline by x-ray diffraction. [d] No —OH or —C—C—CN by infrared analysis. [e] No —OH or —C—C—CN by infrared analysis; approximately 25% crystalline by x-ray diffraction. [f] Polymer from C after extraction with boiling quinoline. [g] Equivalent to an average degree of polymerization of four by assuming two aldehyde end groups per chain or a number-average molecular weight of approximately 1200.

polymer I by the self-condensation of *p*-tolualdehyde. Polymer II was prepared by the copolymerization of terephthalaldehyde and benzene-1,4-diacetonitrile:[19-21]



Results. The solution polymerization of terephthalaldehyde and benzene-1,4-diacetonitrile resulted in the formation of a brightly colored, insoluble, infusible product. Sodium ethoxide, sodium methoxide and piperidine proved to be effective catalysts and absolute ethanol was found to be the best solvent for the reaction. Equimolar mixtures of the monomers with these catalysts gave the polymeric products listed in Table I.

All polymeric products obtained were found to be infusible below the decomposition point and insoluble in a wide variety of solvents at the boiling point, including pyridine, nitrobenzene, dimethyl sulfoxide, *n*-butylaniline, 1-methyl naphthalene, *m*-cresol, *p*-chloroaniline, anthracene, dibenzofuran, quinoline, concentrated sulfuric acid, orthophosphoric acid, and concentrated aqueous zinc chloride. A fluorescence spectrum was obtained for polymer A of Table I. The fluorescence spectrum of this polymer contained only one band centered at about 5800 Å. A low molecular weight analog of polycyanoterephthalylidene, prepared from benzaldehyde and benzene-1,4-diacetonitrile, fluoresced with a pale blue color and a broad band centered at about 4800 Å. This compound, benzene 1,4-bis(α-benzoacetonitrile), was readily soluble in warm benzene and nitrobenzene.

Fusion polymerizations of terephthalaldehyde and benzene-1,4-diacetonitrile also gave infusible and insoluble products. These products ranged from light cream, to red, to black in color.

p-Tolualdehyde could not be polymerized in absolute ethanol solution or in mass using sodium ethoxide, pyridine, or piperidine as catalyst. In both types of reactions, *p*-toluic acid was the principal product.

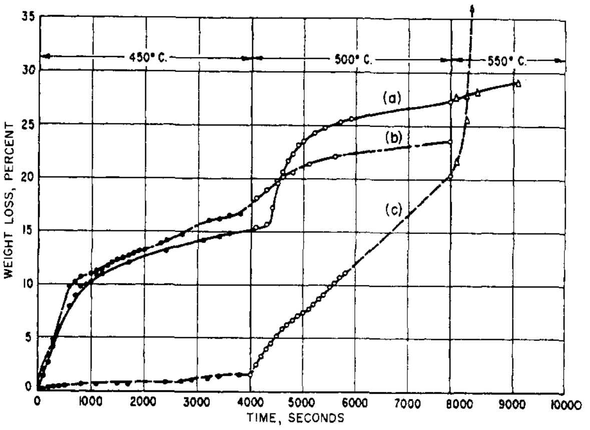


Fig. 1. Thermal gravimetric analyses of (a) polymer C of Table I, (b) polymer D of Table I, (c) polytetrafluoroethylene; weight loss *vs.* time under nitrogen

Thermal degradation studies were made on polycyanoterephthalylidene before and after extraction with boiling quinoline. Measurements were made on the rate of volatilization in a stream of nitrogen at consecutive temperatures of 450°, 500°, and 550° for polymers C and D and for Teflon for comparison, as Teflon is the most stable high polymer containing an all carbon backbone. The results obtained are plotted in Fig. 1. X-ray diffraction patterns and infrared spectra were obtained for polycyanoterephthalylidenes before and after pyrolysis. The infrared spectra of the original extracted polymer D and of this polymer after pyrolysis at 450°, 500°, and 550° consecutively, are shown in Fig. 2. The x-ray diffraction patterns showed that the crystallinity present in the original polymer disappeared completely on pyrolysis at 450°.

Discussion. Several of the polymeric products obtained from the polymerization of terephthalaldehyde and benzene-1,4-diacetonitrile, Table I, had empirical formulas very close to that of the desired repeating unit in polycyanoterephthalylidene, II. The oxygen present appeared to be mostly in the form of aldehyde end groups. Infrared

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(19) L. F. Fieser and M. M. Pechet, *J. Am. Chem. Soc.*, 68, 2577 (1946).

(20) H. Kauffmann, *Ber.*, 523 (1917).

(21) S. Wawzonek and E. M. Smolin, *Org. Syntheses*, Coll. Vol. III, 715 (1955).

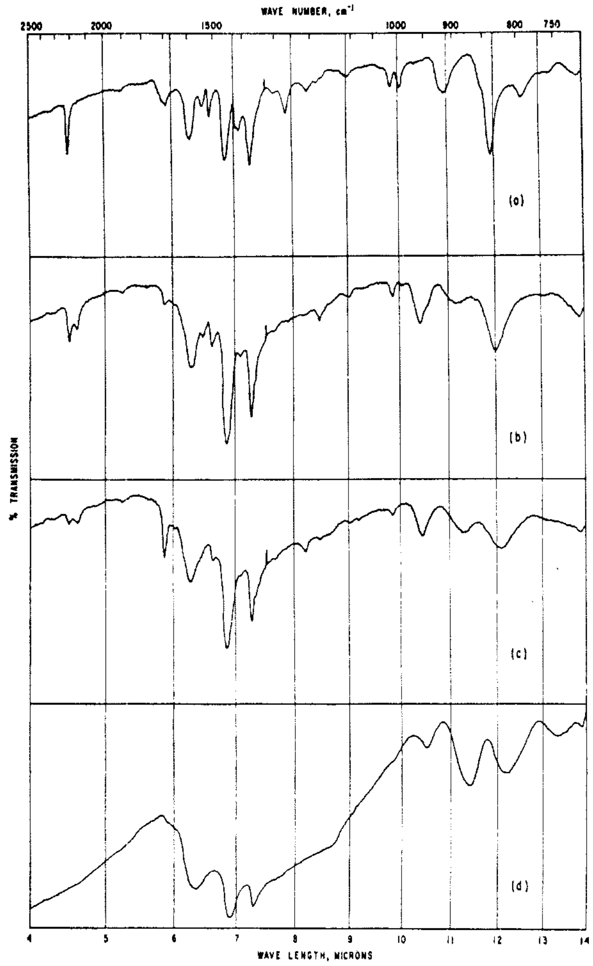


Fig. 2. Infrared spectra of polycyanoterephthalylidenes: (a) polymer C of Table I, (b) same pyrolyzed at 450°, (c) same pyrolyzed at 500°, (d) same pyrolyzed at 550°, (Nujol mulls)

spectroscopic analysis showed that only a very small fraction of the nitrile groups present were on saturated carbon atoms, indicating that the dehydration step went essentially to completion in these reactions and that only negligible amounts of hydroxyl groups were present in the polymers obtained.

The insolubility and infusibility of all of the polymeric materials prepared from both the solution and fusion polymerizations of these monomers suggests that extensive cross-linking occurred in these polymerizations, even though a fairly high order of crystallinity was observed for the polymers. It would not have been surprising, in fact, for the functional groups present in these monomers to have undergone several different types of side reactions. Under the conditions used, reactions which would have led to branching and cross-linking include the Michael addition of hydroxyl or benzylic groups to double bonds in the chain, the Thorpe reaction of these two groups with nitrile functions, and the cyclization of nitrile groups to form trifunctional triazine rings. Other side reactions may have resulted in the formation of thermally-labile linkages especially ester groups, from a Cannizzaro reaction, and carbon-carbon single bonds. Various catalysts, solvents, and reaction temperatures were studied to eliminate or minimize the branching reactions, but in no case was a soluble polymer obtained. The importance of the Cannizzaro reaction is readily apparent from the results of the polymerization studies on *p*-tolualdehyde. The only product isolated in both the solution and fusion runs was *p*-toluic acid even when a weak base, piperidine, was used as the catalyst.

Thermal stability. The thermal gravimetric analyses are presented in the plot of per cent loss in weight *vs.* time in Fig. 1. These curves indicate that polycyanoterephthalylidene was fairly resistant to thermal degradation. Teflon showed very little weight loss (1 to 2%) after one hour at 450°, but rapid decomposition occurred at 500° and complete volatilization ensued at 550°. Polycyanoterephthalylidene, on the other hand, showed a 15 to 20% loss after one hour at 450°, an additional 7 to 12% loss during one hour at 500°, but only an additional 2 to 3% loss after thirty minutes at 550°.

It would not have been possible for this polymer to "unzip" to monomer units or even to any conceivable, simple mixture of low molecular weight, organic products. Volatilization can, therefore, be attributed to one or more of the following effects: (1) low molecular weight polymers were volatilized leaving the high molecular weight fraction of the original polymer; or (2) weak links, built into the polymer chain or pendant to the chain by side reactions, were cleaved, forming volatile polymer fragments or other volatile species, leaving again high molecular weight fragments of the original polymer; or (3) the normal repeating units were being randomly degraded thermally, but the degradation products were largely recombining to form a more stable network structure before complete volatilization occurred.

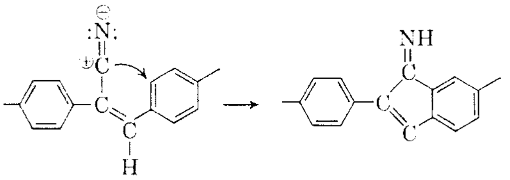
The infrared spectrum of the original polymer was compared with the spectra after heating the polymer at 450°, 500°, and 550°. The infrared spectra of the material heated at 450° and 500° were essentially the same, but had changed considerably when compared to the spectrum of the original. The spectrum of the material heated to 550° indicated that extensive chemical change had occurred on pyrolysis. Considering both weight loss data and the infrared spectra of the polymer samples after successive heat treatments at 450°, 500°, and 550°, the following mechanisms for thermal degradation are offered.

Comparison of the spectra of the original polymer and the polymer heated at 450° indicates that a considerable change in the composition of the polymer had taken place. The weight loss observed at this temperature, therefore, can not be attributed only to the volatilization of low molecular weight polymer, but probably occurred as a result of a chemical or structural changes in the polymer. These changes could have been caused either by scission of weak links originally present in the skeletal structure of the polymer or by thermal decomposition of the normal repeating units through ionic or radical attack, or both. The original polymer, for example, showed no indication from infrared analysis of containing hydroxyl groups, but the polymers heated at 450° and 500° did contain small amounts of these groups.

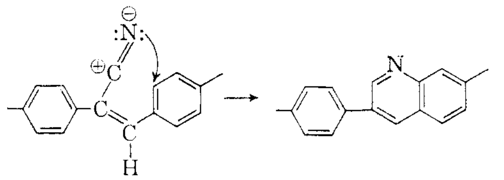
Comparison of the spectra of the samples heated at 450° and 500° indicates that basically little change in composition had occurred between these two temperatures even though a 7 to 12% weight loss was observed. This result indicates that most of the weight loss at 500° can be attributed to the volatilization of low molecular weight fragments which were formed by chemical reactions occurring at or below 450°.

The infrared spectrum of the polymer heated at 550° shows that at that temperature a drastic change had occurred in the molecular structure of the polymer. This material no longer contained measurable amounts of hydroxyl groups, nitrile groups, carbonyl groups, or olefinic double bonds. Closer inspection of all four spectra indicates that actually, the olefin and nitrile groups had been disappearing gradually when the polymers were heated to 450° and 500°. It is quite possible that these changes were caused by attack of the pendant nitrile group on the benzene ring with either, or both, of the following cyclizations occurring:

1. S_E reaction:



2. S_N reaction:



Either reaction would have resulted in the aromatization of the repeating units in the polymer, the first with the formation of iminoindene groups and the second with the formation of quinoline groups. The occurrence of these reactions is indicated, rather convincingly, by the significant increase in intensity of the infrared band at 11.4 microns associated with the presence of lone aromatic hydrogen atoms and the continuous, until complete, disappearance of the band at 11.9–12.2 microns for *p*-phenylene groups.

These reactions should have resulted in the formation of polymeric residues of considerably enhanced thermal stability. The curve in Fig. 1 for the extracted polymer indeed indicates that the residue obtained after heating the polymer at 550° had considerably improved thermal stability over the original polymer. This material showed a weight loss of only 2% after thirty minutes at 550°.

EXPERIMENTAL

Terephthalaldehyde. *p*-Xylene was photobrominated to the tetrabromo derivative and hydrolyzed with dilute sulfuric acid by the procedure of Snell and Weissberger.[22] An overall yield of recrystallized product of approximately 35% was obtained, m.p. 111–112.5°.

Anal. Calcd. for $C_8H_6O_2$: C, 71.5; H, 4.51. Found: C, 71.45; H, 4.46.

Benzene-1,4-diacetonitrile. Three-tenths mole (58 g.) of α,α'-dichloro-*p*-xylene (Eastman Kodak Co.) was dissolved in 350 cc. of 95% ethyl alcohol in a flask and heated to 50°. To this was added dropwise a solution of 0.77 mole (51 g.) of potassium cyanide in 110 cc. of water over a period of 30 min. The solution was then heated at reflux for 90 min. after which the ethyl alcohol was removed by distillation. The residue was combined with 600 cc. of ether and 1 l. of water in a separatory funnel, the ether layer was removed, and the water layer was extracted with three 100-cc. portions of ether. The ether layers were combined and the ether was removed by vacuum distillation on a steam bath. The residue was recrystallized from 95% ethyl alcohol: yield 16 g. (34.1%); m.p. 96–96.5°.

Anal. Calcd. for $C_{10}H_8N_2$: C, 76.9; H, 5.13; N, 17.9. Found: C, 76.79; H, 4.90; N, 17.87.

Polycyanoterephthalylidene. Sodium methoxide catalysis. To a solution of 1.56 g. (0.01 mole) of benzene-1,4-diacetonitrile and 1.34 g. (0.01 mole) of terephthalaldehyde in 200 ml. of ethanol was added dropwise with stirring a solution of 1.5 g. (0.0278 mole) of sodium methoxide (Fisher Scientific Co.) in 25 ml. of ethanol. The color of the reaction mixture changed from clear to bright orange during the addition, and after approximately 15 ml. of the catalyst solution had been added a solid precipitate commenced to form. After addition was complete, the solution was heated to boiling and solvent was distilled off at a slow, steady rate. Concurrently and at approximately the same rate, additional solvent was added dropwise until 250 ml. of solvent had been distilled over a period of approximately 6 hr. The precipitate was collected, washed with ethanol and ether, and dried in a vacuum oven.

Infrared analysis of a Nujol mull of the polymer indicated the presence of approximately 5–10% aldehyde, up to 5% hydroxyl, and a ratio of unsaturated —C═C—CN to saturated —C—C—CN of approximately 30 to 1.

Anal. Calcd. for the repeating unit $C_{18}H_{10}N_2$: C, 85.03; H, 3.94; N, 11.03. Found: C, 74.34; H, 3.98; N, 8.71.

Piperidine catalysis. The polymerization was performed as above but 0.09 g. (0.001 mole) of freshly distilled piperidine was used as the catalyst. A yield of 0.90 g. (35.4%) of a yellow solid was obtained. Infrared analysis of a Nujol mull of the polymer did not indicate any hydroxyl or saturated —C—C—CN present.

Anal. Found: C, 77.85; H, 4.38; N, 8.97.

Sodium ethoxide catalysis. The catalyst was prepared by the addition of 0.20 g. (0.0087 mole) of sodium to 50 ml. of ethanol. This solution was added dropwise to a solution of

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[22] J. M. Snell and A. Weissberger, *Org. Syntheses*, **Coll. Vol. III**, 788 (1955).

2.00 g. (0.015 mole) of terephthalaldehyde and 2.33 g. (0.015 mole) of benzene-1,4-diacetonitrile in 250 ml. of ethanol held at 5° under an atmosphere of nitrogen. When approximately 10 ml. of the catalyst solution had been added the reaction mixture became yellow in color and an orange-yellow solid began to precipitate. Stirring was continued for approximately 16 hr. at 5° then the orange, solid product was filtered, washed with ethanol and ether, and dried in a vacuum oven. Infrared analysis of a Nujol mull indicated the absence of saturated —C—C—CN and hydroxyl groups and the presence of 5–10% aldehyde groups.

Anal. Found: C, 79.32; H, 4.02; N, 10.28.

Two fusion polymerizations were run on this monomer system using sodium methoxide as the catalyst and no solvent. In both experiments, the equimolar monomer mixture was first heated in a sealed glass ampoule under nitrogen. The ampoule was then opened and heating was continued at atmospheric pressure under a stream of nitrogen.

Polyterephthalylidene. The self-condensation of *p*-tolualdehyde was attempted by both solution and mass polymerizations as above. Sodium ethoxide, pyridine, and piperidine were used as catalysts and absolute ethanol as the solvent in the solution runs.

Thermal decomposition measurements. Thermal decomposition measurements were made on polymers C and D and on Teflon for comparison. A tubular electric furnace and a chainomatic balance were incorporated into an apparatus constructed for thermal gravimetric analysis. The polymers were pyrolyzed under a nitrogen atmosphere.

Acknowledgment. The authors wish to express their appreciation to R. A. Nyquist for assistance in obtaining and interpreting the infrared spectra of the polymers.

MIDLAND, MICH.

[COMMUNICATION NO. 2045 FROM THE RESEARCH LABORATORIES, EASTMAN KODAK CO.]

Bisesteramides of Terephthalic Acid

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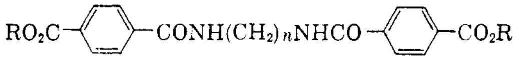
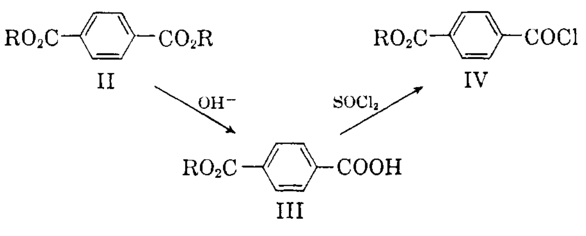
A general synthesis for a new class of bisesteramides I has been devised. Terephthalic esters were hydrolyzed to the ester acids and converted to the acid chlorides which, when treated with the diamine and base, yielded the bisesteramides. Alternate syntheses for specific esteramides are also discussed.

During the investigation of a new class of polyesters, it became necessary to prepare a series of esteramides of the type I.



I

The terephthalic esters (II) were hydrolyzed to the ester acid (III), which, in turn, was converted to the acid chloride (IV) with thionyl chloride.[1] Reaction of two moles of IV with one mole of an aliphatic diamine (V) in the presence of a base gave the required esteramide, I.



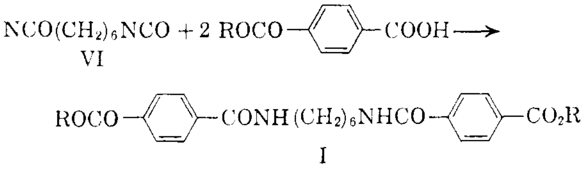
$$2\text{IV} + \underset{\text{V}}{H_2N(CH_2)_nNH_2} \longrightarrow \text{I}$$

The physical constants and analytical data for the bis(4-carboalkoxybenzoyl)alkylenediamines which have been prepared by this method are collected in Table I. Three derivatives of secondary amines are appended at the end of the table.

The required dialkyl terephthalates (II) were prepared by ester interchange from dimethyl terephthalate and the appropriate alcohol using titanium tetrabutoxide as a catalyst.

Formation of the esteramide, I, from IV and V was carried out, using either pyridine or aqueous sodium hydroxide as the acid-acceptor. The latter method was preferred since the use of pyridine led to the formation of colored by-products.

An alternate synthesis of the six carbon esteramides I ($n = 6$) was accomplished by the following isocyanate method:



Where R, = C_2H_5, a yield of 71% was obtained.

During the preparation of *N,N′*-bis(*p*-carbomethoxybenzoyl)hexamethylenediamine, I (n = 6; R = CH_3), a high-melting impurity was isolated. Its formation was favored by long reaction times, high temperatures, and excess isocyanate. The high-melting by-product was more evident during a reaction time of fourteen minutes at 225° than at 175° for an hour and a half. Table II summarizes the reaction conditions and yields of various run in a number of solvents.

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(1) J. B. Cohen and H. S. DePennington, *J. Chem. Soc.*, **113**, 57 (1918).