

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, GENERAL MILLS, INC.]

Cyclic End Groups in Polyamide Resins¹

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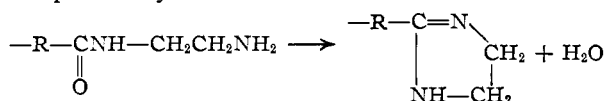
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Infrared absorption techniques have demonstrated that the end groups for certain polyamide resins may be cyclic. The resins studied were based on dimerized, unsaturated vegetable oil acids and short chain di- and polyamines. Whereas resins based on ethylenediamine do not have cyclic end groups, resins prepared with diethylenetriamine have imidazoline end groups. Correspondingly, resins made with 1,3-diaminopropane appear to have only amine end groups, whereas those based on imino-bis-propylamine show evidence of tetrahydropyrimidine end groups.

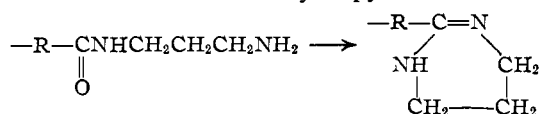
It has generally been assumed that the end groups of polyamide resins are carboxyl and primary amine groups, if the diamine employed is not N-alkylated. Work in this Laboratory, however, indicated the presence of cyclic end groupings in polyamides prepared by treating short chain di- and polyfunctional amines with polymerized, unsaturated vegetable oil fatty acids. Accordingly, an investigation was undertaken to determine if cyclic end groups could be detected qualitatively by infrared absorption spectroscopy.

The polymerized vegetable oil acids employed were predominantly dibasic, although trimers and higher polymers may also be present in varying amounts. Polyamides of this type have been described by Cowan, *et al.*² Also, Anderson and Wheeler³ have discussed the relationship between viscosities and molecular weights of polyamides based on pure dilinoleic acid and ethylenediamine.

If the diamine used for polyamide formation contains amine groups separated by two carbon atoms, the possibility exists for imidazoline formation



If a 1,3-diamine is involved, the possibility exists for the formation of a tetrahydropyrimidine



In both instances a $>\text{C}=\text{N}$ — exists which should provide a characteristic infrared absorption band. Miller⁴ and Colthup⁵ state that this band appears in the range of frequencies of approximately 1660–1610 cm^{-1} .

The spectra of an imidazoline and a tetrahydropyrimidine were examined to obtain bands of reference. The former, 2,4,4-trimethyl-1-isopropyl-2-imidazoline⁶ was found to have an absorption band at 1625 cm^{-1} which may be attributed to the $\text{C}=\text{N}$ grouping. The latter, 2-methyl-3,4,5,6-tetrahydropyrimidine,⁷ demonstrated the presence

of this same linkage by a characteristic absorption band at 1640 cm^{-1} . In addition, a band due to ring N–H deformation at 1545 cm^{-1} was observed.

The spectra of a polyamide prepared with ethylenediamine showed only those bands characteristic of amino-carbonyl (amide) groups. This absorption band is at 1660 cm^{-1} and occurs in all polyamides examined. A second characteristically strong absorption band occurs in the region of 1550–1560 cm^{-1} . This band is due to the N–H deformation vibration of the amide linkage. The N–H linkage of possible amine end groups does not absorb sufficiently to be observed in the absorption spectra of polyamides. No absorption due to acid carbonyl groups could be observed, and titration indicated that carboxyl end groups were normally present to the extent of only about 0.5%.

Any band due to appreciable quantities of the $\text{C}=\text{N}$ — linkage would necessarily be superimposed on the long wave length side of the amide carbonyl band. This band was not present in the spectrum of an ethylenediamine polyamide. The imidazoline structure, however, is clearly present in three polyamides prepared with diethylenetriamine, as shown in Fig. 1, A, B and C. These polyamides had solution viscosities (35% in toluene-butyl alcohol, 1:1) of approximately 92, 75 and 40 centipoises, respectively.

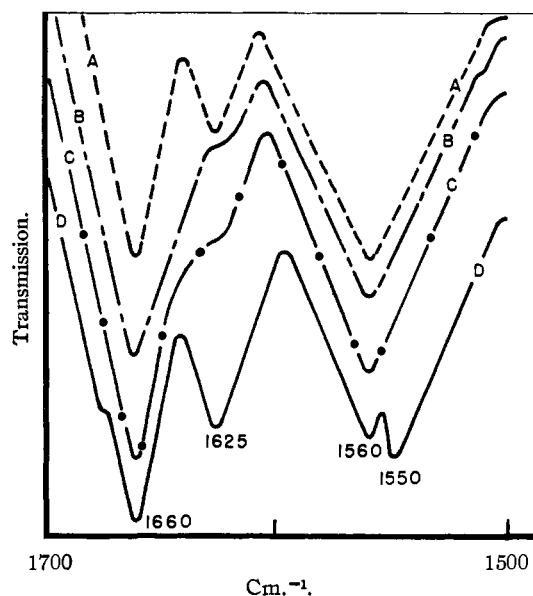


Fig. 1.—Infrared spectra of diethylenetriamine polyamides: A, visc = 40 centipoises; B, visc = 75 centipoises; C, visc = 92 centipoises; D, treated with HCl.

(1) Paper No. 169, Journal Series, General Mills Research Laboratories.

(2) J. C. Cowan, L. B. Falkenberg, H. M. Teeter and P. S. Skell, U. S. Patent 2,450,940 (October 12, 1948).

(3) R. H. Anderson and D. H. Wheeler, *THIS JOURNAL*, **70**, 760 (1948).

(4) F. A. Miller, "Organic Chemistry," Vol. III, edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 145.

(5) N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 398 (1950).

(6) J. L. Riebsomer, *THIS JOURNAL*, **70**, 1629 (1948).

(7) S. Aspinall, *ibid.*, **62**, 2160 (1940).

As would be expected, the intensity of the imidazoline absorption band at 1625 cm^{-1} varied inversely with increasing molecular weight, since higher molecular weight polymers have fewer end groups.

Of interest also is the fact that the treatment of high viscosity diethylenetriamine polyamides with hydrochloric acid, under conditions normally used to prepare imidazolines, yielded a resin whose absorption spectrum indicated the presence of a significantly increased amount of imidazoline. This is demonstrated in Fig. 1D. Conditions of treatment with hydrochloric acid were sufficiently mild to avoid substantial degradation of the polymer. The spectrum showed a band at 1550 cm^{-1} due possibly to N-H deformation of an unsubstituted amide group. Similar treatment of a polyamide prepared with excess ethylenediamine did not produce any imidazoline which could be detected by infrared absorption.

Polyamide resins prepared from 1,3-diaminopropane and 1,3-diaminobutane did not demonstrate the absorption band characteristic of tetrahydropyrimidines. However, a polyamide prepared with imino-bis-propylamine, which is an N-substituted 1,3-diaminopropane, demonstrated a strong absorption band at 1640 cm^{-1} . Thus both N-substituted 1,2- and 1,3-diamines produced polyamides whose end groups were cyclic. Since quantitative work was not performed it was impossible to tell whether all of the end groups in these resins were cyclic.

The difference in ease of ring formation in resins prepared with unsubstituted and N-substituted amines is a source of interesting conjecture. Analogously, other substituted structures are known to favor ring formation. Thus tetramethylsuccinic acid exists only as an anhydride.⁸ Upon treatment with bromine in carbon tetrachloride solution allylacetic acid yields primarily a dibromide, whereas diphenylallylacetic acid, $\text{CH}_2=\text{CHCH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{COOH}$, yields only a bromolactone.⁹

Experimental

Measurement of Infrared Spectra.—The spectrometer used for most of this work was a modified Beckman IR-2 which has been described by Tolberg and Boyd.¹⁰ A few

(8) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 373.

(9) R. T. Arnold, M. de Moura Campos and K. L. Lindsay, THIS JOURNAL, **75**, 1044 (1953).

(10) W. E. Tolberg and H. M. Boyd, *Anal. Chem.*, **24**, 18 (1952).

spectra were recorded on a Beckman IR-3 but the results obtained were interchangeable with those from the smaller instrument. Sample preparation was the same for all polymers. A solution of the sample was deposited dropwise on the surface of a rock salt plate and the solvent was removed by evaporation at 60° . Crystalline materials were milled in mineral oil on the salt plates. Spectra were recorded from 2 to $15\ \mu$.

Preparation of Polyamide Resins.—All polyamide resins used in this study were prepared from commercially available polymerized (dimerized and trimerized) vegetable oil fatty acids, as described by Cowan, *et al.*² Amines used were commercial products which were purified by distillation if necessary. Molar ratios of acids and amines were used except to prepare polymers with lower molecular weights or excess end groups. Here excess quantities of amine were employed.

In a typical preparation 1.0 equiv. (291.8 g.) of polymerized vegetable acids reacted with 1.0 equiv. (39.7 g.) of 75.6% ethylenediamine. These reactants were heated to 200° in a flask equipped with a stirrer, thermometer and 25-cm. Vigreux column. Attached to the column was a distillation take-off and condenser. The reaction mixture was stirred at 200° for 3 hr., and during the last hour a vacuum of 20 mm. was applied.

Properties of the various polyamides prepared are demonstrated in Table I.

TABLE I
PROPERTIES OF POLYAMIDE RESINS

Amine used	Molar ratio of amine to acid	Solution viscosity, centipoises ^a	M.p., °C. Ball and ring ^b
Ethylenediamine	1.0	100	107
Diethylenetriamine	1.0	92	60
Diethylenetriamine	1.05	75	48
Diethylenetriamine	1.10	40	38
1,3-Diaminopropane	1.0	135	54-55
1,3-Diaminobutane	1.0	50	56
Imino-bis-propylamine	1.0	75	56-57

^a 35% solution in butyl alcohol-toluene, 1:1. ^b ASTM standard E28-51T.

Treatment of Diethylenetriamine Polyamide with HCl.—A mixture of 303 g. of the diethylenetriamine resin (Table I) prepared with a molar ratio of amine to acid of 1.0 was treated with 2.0 g. of concd. HCl. Xylene (35 ml.) was added to remove azeotropically water of reaction and the water in the HCl (1.28 ml.). The mixture was stirred and heated to 235° in one hour and kept there for an additional hour. At the end of this time 2.1 g. of water had collected. The xylene was removed *in vacuo* to obtain the product whose spectrum is shown in Fig. 1D.

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