

duced with a Hewlett-Packard model 202-A low-frequency function generator and the spectra obtained on a Varian Associates model V 4300B spectrometer operating at 40.01 mc. Spinning of the sample was always employed unless the signal to noise ratio obtained in the high dilution runs precluded any advantage from this homogenization procedure. Visual observation and measurement of the side bands was carried out on the oscilloscope in some cases, and in the others the Sanborn recorder was employed and the output in c.p.s. counted from the chart paper.

**Sample Preparations.** **Method A**, external standard procedure: Into 5-mm. outside diameter Pyrex tubes were sealed solutions of the substituted fluorobenzene in solvent along with sealed 1-mm. capillaries containing the standard, (a) solution prepared by adding 10 ml. of saturated KOH solution to 40 ml. of saturated KF, (b) neat ( $C_6H_5F$ ). Concentrations of 25, 50, 75 and 100 volume per cent. solute were

prepared within the sample tube by delivering appropriate amounts of the liquids from a 1-ml. syringe; the total volume being 0.4 ml., neglecting small shrinkage effects. The tubes were thoroughly mixed by shaking before examination.

**Method B**, internal standard (5 volume per cent.) procedure: Into 5-mm. o.d. Pyrex tubes were delivered 0.54 ml. of solvent and 0.03 ml. of both  $C_6H_5F$  and the substituted fluorobenzene, the former from a 1-ml. syringe, the latter from a 0.100-ml. syringe. The tubes were sealed and thoroughly shaken before examination. Results are listed in Table XI.

**Acknowledgment.**—We are pleased to acknowledge the valuable assistance of Dr. G. C. Finger in providing the compounds indicated in Table X.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, AMERICAN VISCOSE CORPORATION]

## Isomorphous Replacement in Copolyamide Systems. Homologs of Adipic and Terephthalic Acids

BY ARTHUR J. YU<sup>1</sup> AND ROBERT D. EVANS

RECEIVED APRIL 7, 1959

Four pairs of comonomers—(1) suberic acid/*p*-benzenediacetic acid, (2) sebacic acid/*p*-benzenedipropionic acid, (3) hexamethylenediamine/*p*-xylene- $\alpha,\alpha'$ -diamine, (4) octamethylene-diamine/2,2'-*p*-phenylene-bis-ethylamine—were used to prepare a series of copolyamides. Comonomer pairs 1 and 2 can be considered as homologs of adipic and terephthalic acids; comonomer pairs 3 and 4 are the amino analogs of 1 and 2. The members of each pair bear the same structural relationship as adipic and terephthalic acids. It was found that copolyamides containing comonomer pairs 2 and 4, in which the number of methylene groups between the benzene ring and the functional groups is even, were isomorphous, whereas copolyamides containing comonomer pairs 1 and 3, in which the number of methylene group is odd, were not isomorphous. A lattice model for crystallization of copolyamides was proposed to correlate the experimental results.

### Introduction

Isomorphous replacement of adipic and terephthalic acids in copolyamide systems was first suggested by Edgar and Hill.<sup>2</sup> Our work, reported elsewhere,<sup>3</sup> has substantiated this finding, and also established the effect of diamine structure on the isomorphism of these two diacids. In general, adipic and terephthalic acids will form isomorphous copolyamide systems with straight chain aliphatic diamines. The melting point *vs.* composition curves of these systems are sigmoidal and have no minimum at the intermediate ranges of composition. Since the structural difference of adipic and terephthalic acids involves the separation of carboxyl groups in the former by four methylene groups, and in the latter by a *p*-phenylene unit, it is the purpose of this work to investigate whether other comonomer pairs, with the same structural difference as adipic and terephthalic acids, can also be isomorphous in copolyamide systems. Four pairs of comonomers were selected: (1) suberic acid and *p*-benzenediacetic acid, (2) sebacic acid and *p*-benzenedipropionic acid, (3) hexamethylenediamine and *p*-xylene- $\alpha,\alpha'$ -diamine, and (4) octamethylenediamine and 2,2'-bis-phenylene-bis-ethylamine.

Comonomer pairs 1 and 2 can be considered as homologs of adipic and terephthalic acids. Comonomer pairs 3 and 4 are the amino analogs of 1 and 2. Copolyamides were prepared from these

comonomer pairs with aliphatic straight chain diamines or diacids, and a melting point *vs.* composition curve was plotted for each system. The presence or absence of minima in these curves will indicate the isomorphous replacement of four methylene groups by a *p*-phenylene unit in the copolyamide systems under study. This information could lead to the understanding of the mechanism of polymer isomorphism.

### Experimental

**Chemicals.**—Adipic acid, suberic acid, azelaic acid, sebacic acid, hexamethylenediamine and octamethylenediamine were purchased.

*p*-Benzenediacetic acid, m.p. 250–252°, was prepared by the method of Kipping,<sup>4</sup> except  $\alpha,\alpha'$ -dichloro-*p*-xylene was used instead of the corresponding dibromo compound.

*p*-Benzenedipropionic acid, m.p. 232°, was prepared by the catalytic hydrogenation of *p*-benzenediacrylic acid<sup>5</sup> in sodium hydroxide solution.

*p*-Xylene- $\alpha,\alpha'$ -diamine was prepared from  $\alpha,\alpha'$ -dichloro-*p*-xylene and hexamethylenetetramine. A mixture of 280 g. (2 moles) of hexamethylenetetramine, 176 g. (1 mole) of  $\alpha,\alpha'$ -dichloro-*p*-xylene and 3.5 l. of chloroform was refluxed for 3 hr. to give 403 g. (89%) of the di-quaternary hexaminium salt. The quaternary salt was warmed at 50° with stirring in 3 l. of absolute ethanol containing about 300 g. of anhydrous hydrogen chloride. After the diamine di-hydrochloride precipitated, the mixture was refluxed for 3 hr. The diamine di-hydrochloride was then collected, dried, and dissolved portionwise in excess sodium hydroxide solution. The organic layer was extracted with benzene. Removal of benzene gave 115 g. (95% based on the quaternary hexaminium salt) of crude *p*-xylene- $\alpha,\alpha'$ -diamine. Distillation under reduced pressure gave the purified product, b.p. 120–123° (0.5 mm.), m.p. 44–46°. *Anal.* Calcd. for  $C_8H_{12}N_2$ : C,

(1) Thiokol Chemical Corporation, Trenton, N. J.

(2) O. B. Edgar and R. Hill, *J. Polymer Sci.*, **8**, 1 (1952).

(3) A. J. Yu and R. D. Evans, presented at the 135th American Chemical Society Meeting, Boston, Mass., 1959.

(4) J. S. Kipping, *Ber.*, **21**, 42 (1888).

(5) P. Ruggli and W. Theilheimer, *Helv. Chim. Acta*, **24**, 899 (1941).

TABLE I  
 MELTING POINTS AND ANALYSES OF NYLON SALTS

Diamine	Nylon salts	Diacid	M.p., °C.	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
Hexamethylenediamine	Adipic		196	$C_{12}H_{26}N_2O_4$	54.93	54.98	9.99	10.13	10.68	10.84
	Sebacic		175	$C_{18}H_{34}N_2O_4$	60.34	60.30	10.76	10.89	8.80	9.02
	<i>p</i> -Benzenediacetic		259	$C_{16}H_{26}N_2O_4$	61.91	61.95	8.44	8.47	9.03	9.50
Octamethylenediamine	Adipic		155	$C_{14}H_{30}N_2O_4$	57.90	57.89	10.41	10.09	9.65	10.01
	Suberic		191	$C_{16}H_{34}N_2O_4$	60.34	60.58	10.76	10.18	8.80	9.02
	Azelaic		161	$C_{17}H_{36}N_2O_4$	61.40	61.34	10.91	10.75	8.43	8.35
	<i>p</i> -Benzenediacetic		226	$C_{18}H_{30}N_2O_4$	63.88	63.86	8.93	8.57	8.28	8.70
	<i>p</i> -Benzenedipropionic acid		200	$C_8H_{24}N_2O_4$	65.54	65.32	9.35	9.70	7.65	7.58
<i>p</i> -Xylene- $\alpha, \alpha'$ -diamine	Sebacic		175	$C_{18}H_{34}N_2O_4$	62.39	62.51	11.05	11.17	8.09	7.99
	Adipic		308	$C_{14}H_{22}N_2O_4$	59.54	59.52	7.86	7.77	9.92	9.32
2,2'- <i>p</i> -Phenylene-bis-ethylamine	Sebacic		215	$C_{18}H_{30}N_2O_4$	63.88	63.57	8.93	9.02	8.28	8.15
	Adipic		202	$C_{16}H_{26}N_2O_4$	61.93	61.61	8.44	8.41	9.03	9.06
	Suberic		207	$C_{18}H_{30}N_2O_4$	63.88	63.99	8.93	9.17	8.28	8.31
	Azelaic		197	$C_{19}H_{32}N_2O_4$	64.74	64.65	9.15	9.36	7.95	8.42
	Sebacic		210	$C_{20}H_{34}N_2O_4$	65.54	65.32	9.35	9.39	7.65	7.87

70.54; H, 8.88; N, 20.57. Found: C, 70.37; H, 9.11; N, 20.38.

2,2'-*p*-Phenylene-bis-ethylamine, b.p. 130° (3 mm.), was prepared by the method of Ruggli and co-workers.<sup>6</sup>

**Preparation of Polymers.**—The polyamides and copolyamides were prepared by the method previously described.<sup>3</sup> Generally, a neutral nylon salt was prepared from a diamine and a diacid in ethanolic solutions, and the polymer was obtained by heating the salt under nitrogen and then under reduced pressure, to a high degree of polymerization. The melting points and elemental analysis of the nylon salts prepared in this work were listed in Table I.

**Determination of Polymer Melting Point.**—The melting points were determined by observing solid particles of the polymer between crossed Nicol polarizers on an electrically heated hot-stage microscope. The temperature at which the last trace of birefringent crystallinity completely disappeared was taken as the melting point.

### Results and Discussion

All the copolyamides were crystalline, as evidenced by their optical birefringence. Plots of melting point against copolymer composition are shown in Figs. 1-4. The curves thus obtained can

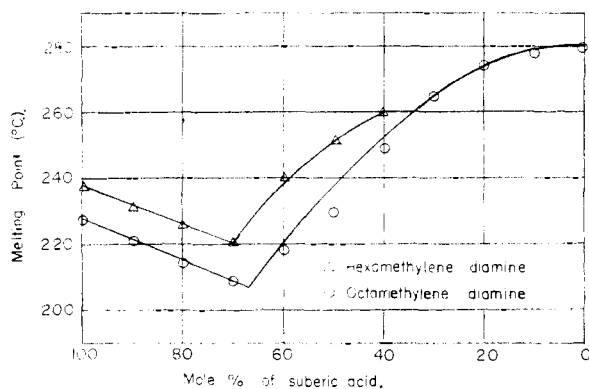


Fig. 1.—Copolyamides of suberic acid and *p*-benzenediacetic acid.

be divided into (1) the sigmoidal curve with no minimum and (2) the "V" curve with its eutectic point at some intermediate composition. Since the absence of a minimum is taken as the criterion of polymer isomorphism, the four comonomer pairs can be classified either as isomorphous or non-isomorphous: isomorphous systems: (1) sebacic acid

(6) P. Ruggli, B. B. Bussemaker, Wilhelm Müller and A. Staub, *Helv. Chim. Acta.*, **18**, 1388 (1935).

and *p*-benzenedipropionic acid, (2) octamethylenediamine and 2,2'-*p*-phenylene-bis-ethylamine; non-isomorphous systems: (1) suberic acid and *p*-benzenediacetic acid, (2) hexamethylenediamine and *p*-xylene- $\alpha, \alpha'$ -diamine.

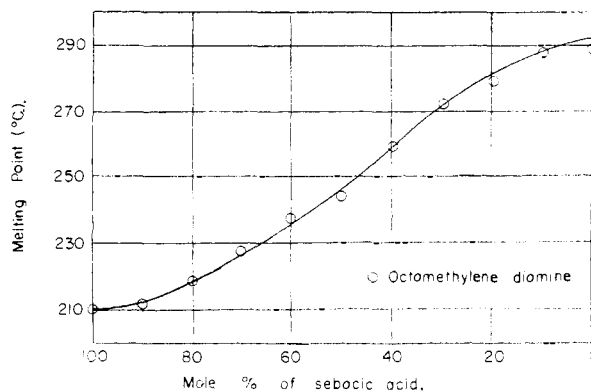


Fig. 2.—Copolyamide of sebacic acid and *p*-benzenedipropionic acid.

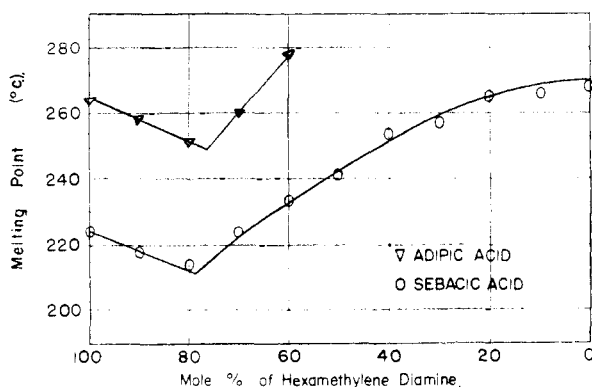


Fig. 3.—Copolyamides of hexamethylenediamine and *p*-xylene- $\alpha, \alpha'$ -diamine.

These results show: (1) that four methylene groups and a *p*-phenylene unit are not always isomorphically replaceable in copolyamide systems, (2) that adipic and terephthalic acids are not unique as an isomorphous comonomer pair in

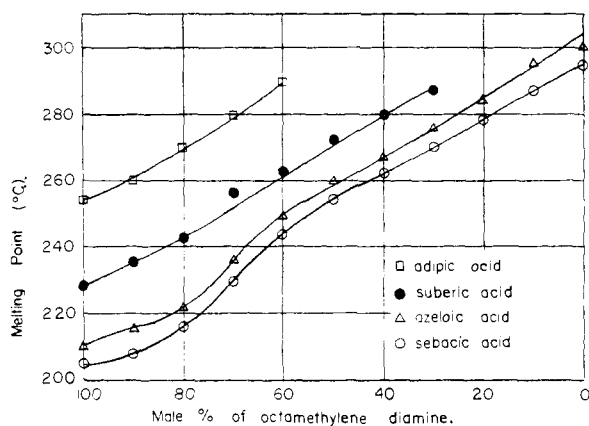


Fig. 4.—Copolyamides of octamethylenediamine and 2,2'-*p*-phenylene-bis-ethylamine.

which one member is aliphatic and the other aromatic.

A proposed model for copolyamide crystallization which is able to correlate the experimental results follows. Consider first the crystalline structure of poly-(hexamethylene adipamide). Bunn and Gardner<sup>7</sup> have shown that the polymer chains, each assuming a fully extended planar configuration, are so arranged that the -NH of one chain is always opposite to the >C=O of a neighboring chain. The hydrogen bonds thus formed bind the chains together, as shown in Fig. 5, into a flat sheet

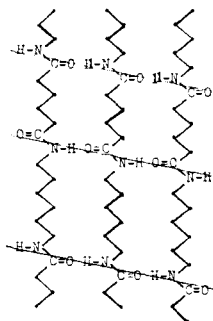


Fig. 5.—Schematic drawing of chain alignment and dipole association in poly-(hexamethylene adipamide).

on which the polyamide backbones lie. These sheets of polymer will then stack into layers to form the crystallites. Baker and Fuller<sup>8</sup> suggested these hydrogen bonds associate to form parallel dipole layers, which tilt to the chain axis, and extend across the polymeric chains continuously. If these views are combined and extended into three dimensions, one arrives at the model schematically represented in Fig. 6. Here the XZ plane represents the real polymer sheet on which all planar zigzag chains lie, and the XY plane represents the imaginary dipole layer passing through the amide linkages. The intersection of vertical chains with the dipole layers is the lattice point to which the dipoles of the amide must be confined. This model for crystallites of polyamides can be separated into chains and a number of parallel dipole planes on which the lattice points are periodically distributed.

(7) C. W. Bunn and E. V. Gardner, *Proc. Roy. Soc. (London)*, **A189**, 39 (1947).

(8) W. O. Baker and C. S. Fuller, *THIS JOURNAL*, **64**, 2399 (1942).

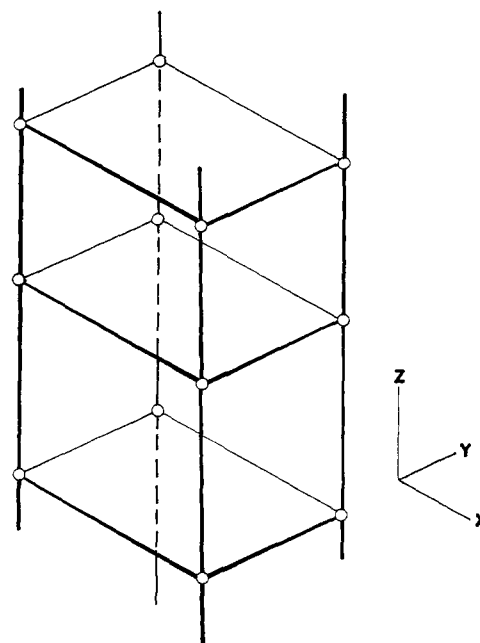


Fig. 6.—Three-dimensional lattice model for crystallization of polyamides and copolyamides.

Thus crystallization will be reduced to a process of fitting the chains into the model with the sole restriction that each amide linkage on the chain must coincide with the lattice point on the dipole planes.

This model will now be used for copolyamide systems. If a chain with the new comonomer distributed at random is fed into this model, when one of the amide linkages of the comonomer under consideration is on the lattice point, any one and only one of the following three conditions could occur to the other amide linkage: (1) It will coincide exactly with the corresponding lattice point on the next dipole plane. (2) It cannot coincide with the lattice point, but still is on the next dipole plane. (3) It cannot coincide with the lattice point, and is displaced out of the dipole plane.

It appeared that all the known isomorphous copolyamides can be described by either condition 1 or 2, while all the known non-isomorphous copolyamides by condition 3.

**Isomorphous Copolyamides.**—For condition 1 to occur, the comonomers must be nearly identical in dimension and configuration. Cramer and Beaman<sup>9</sup> reported that heptamethylenediamine and bis-(3-aminopropyl) ether formed a nearly perfect isomorphous copolyamide with adipic acid. The replacement of a methylene group by an ether oxygen should not result in any critical deviation in comonomer dimension and configuration, hence both units can enter the same lattice.

Condition 2, as stated above, can be illustrated by the isomorphous replacement of adipic acid by terephthalic acid. Consider the orientation and displacement of four methylene groups and a *p*-phenylene unit in the lattice model. In order that all amide linkages, in spite of their origins, can assume the same orientation and thus align properly,

(9) F. B. Cramer and R. G. Beaman, *J. Polymer Sci.*, **21**, 237 (1956).

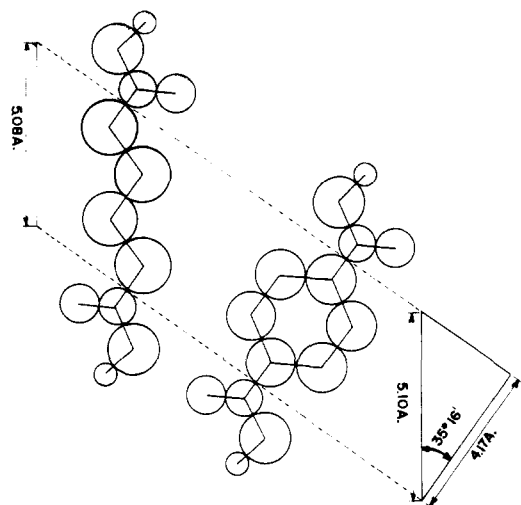


Fig. 7.—Diagram of adipic acid and terephthalic acid showing orientation and displacement of four methylene groups and a *p*-phenylene unit in the lattice model.

the benzene axis must incline at an angle of  $35^{\circ} 16'$  with the chain axis, as shown in Fig. 7. This angle, which is the difference between a right angle and half a tetrahedral angle, is probably the preferred orientation of benzene nuclei in the lattice. From standard bond angles and atomic radii, benzene has an end-to-end length of  $4.17 \text{ \AA}$ . This distance, at an angle of  $35^{\circ} 16'$ , is equivalent to  $5.10 \text{ \AA}$  along the chain axis

$$4.17 \text{ \AA} \times \frac{1}{\cos 35^{\circ} 16'} = 5.10 \text{ \AA}$$

Four methylene groups displace  $5.08 \text{ \AA}$ . This nearly equal axial displacement of these structural units is important; it enables all the amide linkages, whether they belong to adipic acid or terephthalic acid, to fall on the parallel dipole planes of the model. The schematic chain alignment is shown in Fig. 8; AB represents adipic acid and CD

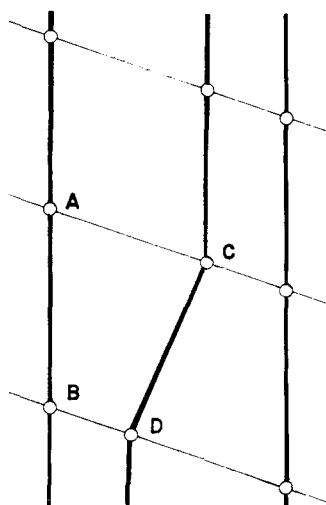
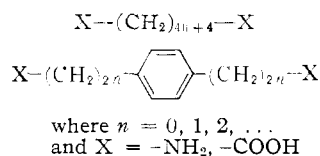


Fig. 8.—Schematic chain alignment of copolyamide of adipic acid and terephthalic acid.

represents terephthalic acid. Both chain segments can fit the lattice model with all the amide

linkages on the dipole planes. There will be some change in the relative location of amide linkages on the dipole plane, but there is no change in the number of amide linkages per unit area of the dipole plane. Although such a lattice, containing both acids, might be defective, the continuous association of hydrogen bonds across the chains can be retained. Thus, the mechanism of isomorphous replacement of adipic and terephthalic acids in copolyamide systems can be conceived by this proposed lattice model. For the homologs of adipic and terephthalic acids, or their amino analogs, the same conditions for chain alignment can arise when, and only when, the number of methylene groups between the benzene ring and the functional groups is even. The case with odd number of methylene groups will be discussed later. It can be deduced that a comonomer pair, if the structure of which can be represented by the formula



probably will exhibit isomorphism, provided the other component has no adverse effect on chain packing. Thus it has been experimentally shown that when  $n$  is 0 and  $X$  is  $-\text{COOH}$  and when  $n$  is 1 and  $X$  is  $-\text{COOH}$  and is  $-\text{NH}_2$ , polymer isomorphism occurred.

**Non-isomorphous Copolyamides.**—Consider the case of suberic acid and *p*-benzenedicetic acid, in which the number of methylene groups between the benzene ring and the functional group is odd. The two diacids still displace nearly equal distance along the chain axis, as does any comonomer pair bearing the same structural relationship as adipic and terephthalic acids. However, the odd number of methylene group has oriented the benzene axis to the opposite direction with respect to the chain axis. As shown in Fig. 9, the amide linkages can no longer coincide with the lattice point. This misfit of amide linkages will perpetuate along the rest of the chain. When this situation arises, the proposed lattice model has predicted that crystallization of both units in the same lattice cannot occur. Thus, the nearly equal displacement of four methylene groups and a *p*-phenylene unit along the chain axis is a necessary but not sufficient condition for polymer isomorphism to occur. The other necessary condition is the correct orientation of the comonomer units in the lattice. The better known examples of nonisomorphous systems are those where comonomer pairs of the same orientation but of different length are used, such as adipic and sebacic acids. In all cases, the continuous association of hydrogen bonds across the polymeric chains is disrupted.

**Partially Isomorphous Copolyamides.**—Partial isomorphism may be defined as the phenomenon that, in a copolymer system containing the comonomers A and B, A can enter the crystalline lattice of B to some extent, but B cannot enter the lattice of A. The existence of partial polymer isomor-

phism is suggested by the shape of the curves in Figs. 1 and 3. As can be seen from the portions of the curves at the right of the eutectics, the initial addition of aliphatic comonomer to the aryl homopolymer did not immediately produce a linear depression of the melting point. This seems to indicate that, within the range of composition covered by the curvilinear portion of the curves, isomorphism could have occurred. To use suberic acid and *p*-benzenediacetic acid as an example, partial isomorphism will signify that, at low molar ratios, suberic acid can enter the crystalline lattice of *p*-benzenediacetic acid. This is not an unreasonable explanation, since it is conceivable to rotate the bonds of a flexible molecule in order to fit the lattice of a rigid one, but not conversely. However, rotating a comonomer molecule out of its most stable configuration will introduce a strain to the lattice, which increases with increased replacement. When the strain surpasses the lattice stability, non-isomorphism and a linear depression of melting point will ensue.

**Acknowledgment.**—The authors are indebted to Drs. J. A. Howsmon and M. R. Lytton for their interest and encouragement in this work. Thanks are due to Dr. J. T. Massengale for organic syn-

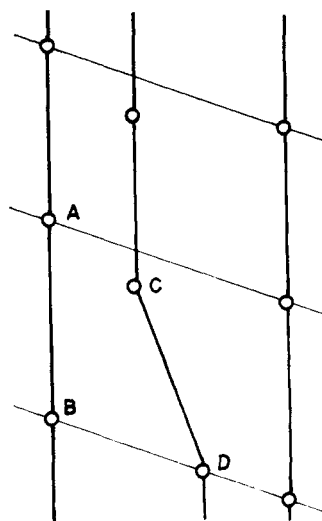


Fig. 9.—Schematic chain alignment of copolyamide of suberic acid and *p*-benzenediacetic acid. AB represents suberic acid and CD *p*-benzenediacetic acid.

thesis, and to Mr. F. F. Morehead for the determination of polymer melting points.

MARCUS HOOK, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

## Organic Reactions under High Pressure. V. The Decomposition of Di-*t*-butyl Peroxide<sup>1</sup>

BY CHEVES WALLING AND GERSHON METZGER

RECEIVED MARCH 23, 1959

The effect of pressures up to 7300 kg./cm.<sup>2</sup> on the decomposition of di-*t*-butyl peroxide at 120° has been studied in four solvents. In all, the rate is depressed by pressure, and values of  $\Delta V^\ddagger$  are calculated in cc./mole as 5.4 (toluene), 6.7 (cyclohexene), 12.6 (benzene) and 13.3 (CCl<sub>4</sub>). The variation has been interpreted as arising from the competition between recombination of *t*-butoxy radicals, attack on solvent (both within the solvent cage) and diffusion out of the cage.  $\Delta V^\ddagger$  for diffusion is apparently <8 cc./mole. The ratio of *t*-butyl alcohol to acetone produced in toluene increases with pressure with the difference in  $\Delta V^\ddagger$  for the two processes being 8.9 cc./mole.  $\Delta V^\ddagger$  for hydrogen abstraction is estimated as -3 to -6 cc./mole. In benzene, toluene has been detected as a reaction product.

Di-*t*-butyl peroxide provides a particularly convenient source of free radicals in the temperature range of 100–150° since it decomposes by a clean unimolecular path at a rate which is almost independent of solvent to yield the highly reactive *t*-butoxy radical.<sup>2</sup> Accordingly, as part of our general program for the investigation of the effect of high pressures on free radical processes, it appeared desirable to study the effect of pressure upon di-*t*-butyl peroxide decomposition as a basis for interpreting pressure effects in radical chain reactions in which it is employed as an initiator.

In general, homolytic dissociation processes might be expected to be retarded by pressure, since the over-all reaction is accompanied by an increase in volume which should be partially achieved in the transition state. Accordingly in

the relation

$$d \ln k/dP = -\Delta V^\ddagger/RT \quad (1)$$

the quantity  $\Delta V^\ddagger$  (the difference in volume between transition state and reactants) should be positive. Previous work in this Laboratory has shown such a retardation by pressure in the case of benzoyl peroxide<sup>3</sup> (although, at higher pressures the rate rises presumably due to induced decomposition) and qualitatively similar results have been reported by Nicholson and Norrish,<sup>4</sup> and, for azobisisobutyronitrile, by Ewald.<sup>5</sup>

Measurements reported here on di-*t*-butyl peroxide were made at 120° in four solvents, benzene, toluene, cyclohexene and carbon tetrachloride, at pressures up to 7300 kg./cm.<sup>2</sup>. In every case the decomposition was retarded by pressure, but values of  $\Delta V^\ddagger$  were found to vary markedly with

(1) Taken from the Ph.D. dissertation of Gershon Metzger, Columbia University, 1958. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

(2) For a review of previous literature, cf. C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 469–472.

(3) (a) C. Walling and J. Pellon, *THIS JOURNAL*, **79**, 4782 (1957); (b) **79**, 4786 (1957).

(4) A. E. Nicholson and R. G. W. Norrish, *Disc. Faraday Soc.*, **22**, 97 (1956).

(5) A. H. Ewald, *ibid.*, **22**, 138 (1956).