cohol. Two small crops of white, felty needles, m. p. 203-205° after recrystallization, were obtained. A mixed melting point with dibenzaldiaminoguanidine nitrate was the same. Further evaporation of the alcohol solution yielded no more crystalline material and left a reddish-brown oil from which a small amount of benzalazine was extracted by trituration with diethyl ether. Other attempts to purify the oil by crystallization failed. Further separation of the compounds in this oil was accomplished by precipitating solid picrates from alcoholic solution. Fractionation of these picrates gave two materials: (1) A compound which was only sparingly soluble in boiling 95% ethyl alcohol and which decomposed at 241–243° after one recrystallization; a mixed melting point with a sample of dibenzaldiaminoguanidine picrate was 241°. (2) A picrate which was readily soluble in hot ethanol and which decomposed at 161–162° after two recrystallizations; a mixed melting point with an authentic sample of benzal-1-*n*-butyl-3-aminoguanidine picrate was 166–167°.

Benzal 1-*n*-Butyl-3-aminoguanidine Picrate.—Twenty-one milliliters of glacial acetic acid was added dropwise during twenty minutes to a slurry of 8.0 g. of 1-*n*-butyl-3-nitroguanidine (0.05 mole), 13.0 g. of zinc dust, and 75 ml. of water. The mixture was vigorously stirred and the temperature maintained at 30–35°. The agitation was continued for twenty minutes longer before the colorless solution was filtered from a small quantity of unreacted zinc. The filtrate was acidified with 5 ml. of concentrated nitric acid (sp. gr. 1.4), warmed to 60°, and shaken with 5 ml. of benzaldehyde. A pink colored viscous oil separated after overnight cooling at 0°. The aqueous layer was decanted and discarded and the oil dissolved in 60 ml. of 95% ethyl alcohol. This latter solution was added to a boiling solution of 10 g. of picric acid in 100 ml. of 95% ethyl alcohol. The yield of solid picrate, m. p. 167–168.5°, crystallizing from the cooled solution was 11.4 g. (39.5%). Recrystallization from 95% ethanol did not change the melting point.

Anal. Calcd. for $C_{18}H_{21}O_7N_7$: C, 48.32; H, 4.73; N, 21.92. Found: C, 48.46, 48.36; H, 4.82, 4.73; N, 22.31, 22.38.

Reaction of Hydrazine Hydrate and 1-Methyl-3-nitroguanidine.—Ten grams of methylnitroguanidine[4] (0.085 mole), 5.0 g. of hydrazine hydrate (0.1 mole), and 50 ml. of water were heated at 65–70° for thirty minutes. Ammonia and nitrous oxide were evolved and the solution became deep orange in color. The solution was cooled, neutralized with 115 ml. of 1 *N* sulfuric acid, and diluted with 95% ethanol until a turbidity developed. Chilling this solution at 0 to 5° yielded 6.5 g. of orange-colored crystals, melting at 205°. The impure product was purified by redissolving in a 25 ml. of water, filtering, diluting the filtrate with 95% ethanol until a turbidity developed, and chilling at 0°. Three recrystallizations gave a white product melting sharply at 227–228°.

Anal. Calcd. for diaminoguanidine sulfate, $2CH_7N_5 \cdot H_2SO_4$: S, 11.60. Found: S, 11.72, 11.76.

The purified sulfate gave a picrate from water solution which melted at 188° after recrystallization from alcohol. A mixed melting point with a sample of diaminoguanidine picrate[8] was also 188°.

Summary

1. The principal products formed in the hydrazinolysis of nitroguanidine in aqueous solution are nitroaminoguanidine, aminoguanidine and diaminoguanidine.

2. The hydrazinolysis of nitroaminoguanidine gives diaminoguanidine.

3. The hydrazinolysis of 1-*n*-butyl-3-nitroguanidine in aqueous solution gives nitroaminoguanidine and diaminoguanidine. In ethyl alcohol 1-*n*-butyl-3-aminoguanidine and diaminoguanidine are formed.

[8] Pellizzari and Cantoni, *Ber.*, **38**, 293 (1905), reported a m. p. of 191°.

CHINA LAKE, CALIFORNIA RECEIVED SEPTEMBER 13, 1949

[CONTRIBUTION NO. 167 FROM THE GOODYEAR RESEARCH LABORATORIES]

Crystallization in High Polymers. V. Dependence of Melting Temperatures of Polyesters and Polyamides on Composition and Molecular Weight[1,2]

BY ROBERT D. EVANS, HAROLD R. MIGHTON[3a] AND PAUL J. FLORY[3b]

In the preceding paper[4] of this series a general treatment of the configurational statistics of semicrystalline polymers was developed on the assumption that the crystalline and amorphous regions, or zones, are separated by distinct boundaries such as those normally occurring between contiguous phases of heterogeneous substances. The theory leads to the concept of an equilibrium melting temperature T_m at which crystallinity disappears completely, this temperature being characteristic of a given polymer in the same way that the melting point of a crystalline compound is characteristic of the substance. Although melting may take place over a range of temperatures preceding T_m, final disappearance of crystallinity is predicted to occur at a definitive temperature above which finite amounts of crystallinity become thermodynamically unstable.

Of the various deductions which follow from the theory,[4] those pertaining to the dependence of T_m on composition are most provocative of experiment. Three such relationships have been derived, expressing, respectively, the dependence of T_m on copolymer composition, on polymer chain length and on degree of dilution with a low molecular weight diluent. Thus, the melting temperature of a random copolymer was predicted to depend on its composition in accordance with the relationship

$$1/T_m - 1/T_m^0 = -(R/h_u) \ln X_A \qquad (1)$$

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[1] The work presented in this paper comprises a part of a program of fundamental research on rubber and plastics carried out under contract between the Office of Naval Research and the Goodyear Tire and Rubber Company.

[2] Presented before the High Polymer Forum at the 112th Meeting of the American Chemical Society, New York, New York, September 16, 1947.

[3] (a) E. J. du Pont de Nemours and Co., Buffalo, N. Y.; (b) Department of Chemistry, Cornell University, Ithaca, New York.

[4] P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).

where X_A is the "mole" fraction of the repeating unit A capable of crystallizing, h_u is the heat of fusion per repeating unit, T_m is the melting temperature as defined above (*i. e.*, the temperature for complete disappearance of crystallinity) and T_m^0 is the melting temperature for the pure polymer composed exclusively of A units ($X_A = 1$) The melting temperature of linear polymers possessing the "most probable" molecular weight distribution was related to the chain length as follows

$$1/T_m - 1/T_m^0 = -2R/h_u\bar{x}_n \qquad (2)$$

where $\bar{x}_n$ is the number average number of repeating units per molecule and T_m^0 represents the melting temperature for infinite molecular weight. Finally, the effect of a diluent on T_m was expressed as follows, assuming $\bar{x}_n$ to be very large

$$1/T_m - 1/T_m^0 = (R/h_u)\ [(z/z_s)(1 - v_2) - \mu(1 - v_2)^2] \qquad (3)$$

where z/z_s is the ratio of the molar volumes of the repeating unit and the diluent, v_2 is the volume fraction of polymer and μ is the energy of mixing parameter equal to BV/RT where B is a constant characteristic of the polymer-diluent pair and V is the molar volume of the repeating unit.

In deriving equation (1), the co-ingredient(s) copolymerized with the repeating unit A has been assumed to be of such a nature as to be unable to enter the crystal arrangement characteristic of A. Likewise, the derivations of equations (2) and (3) rest on the analogous assumptions that the end groups and the diluent, respectively, are excluded from the crystallites. The present investigation has been concerned in part with the validity of these specific assumptions. It will be noted from the above relationships that the co-ingredients in copolymers, the end-groups in polymers of low molecular weight, and the diluent in polymer–diluent mixtures affect T_m in a manner closely analogous to the influence of impurities on the melting of simple substances.[5] The repeating unit of the polymer chain occupies a role corresponding to that of the molecule in the crystallization of monomeric substances.

Linear condensation polymers, such as the polyesters and polyamides, are ideally suited for investigations on the applicability of the above melting temperature relationships. Most of them are capable of exhibiting crystallinity, their melting points are conveniently distributed over a wide range of temperatures,[6] copolymers in which the arrangement of the units is random are easily prepared, and the molecular weight distribution normally obtained is the most probable one. Decrease in T_m with increasing proportions of a co-ingredient has been well established in a number of cases.[7,8] Catlin, Czerwin and Wiley[9] recently reported data on the melting temperatures of copolyamides which exhibit eutectic type of minima at intermediate compositions. This behavior, analogous to that of simple binary systems, is implied by equation (1) for cases in which each of the copolymer ingredients is crystalline when polymerized alone.

In the work reported in this paper[10] melting temperatures of linear copolyesters and copolyamides were systematically investigated as functions of composition. The influence of average molecular weight, nature of the end-groups, and dilution on the melting temperature of decamethylene adipate has been observed as well. The melting temperatures of the polymers and copolymers have been determined by a method which appears to yield a generally satisfactory approximation to the equilibrium T_m.

Experimental

Materials.—Decamethylene glycol, prepared by hydrogenating butyl sebacate over copper chromite[11] followed by treatment with 20% aqueous sodium hydroxide to remove unreduced ester, was recrystallized twice from dry ethylene dichloride; m. p. 72–73.5° (uncor.). Pentamethylene glycol[12] was subjected to a single fractionation, b. p. 130–131° at 9 mm. Commercial diethylene glycol was distilled twice before use. Tetramethylene glycol was purified by distillation followed by two crystallizations from an anhydrous mixture of ether and acetone, the last traces of solvent being removed by distillation. The final product froze at 20.0°. *cis*-1,4-Cyclohexanediol was prepared from hydroquinone by the method of Adkins and Cramer,[13] m. p. 100–102°.

Sebacyl and adipyl chlorides were prepared from the carefully purified acids by treatment with excess thionyl chloride. The crude products were distilled from the reaction mixture at reduced pressure, and subsequently fractionated through an efficient column. Adipyl chloride discolored on standing, and therefore was freshly distilled before use. α-Naphthoyl chloride was similarly prepared from α-naphthoic acid, the fraction distilling from 131–133° at 1 mm. being retained for use. Isophthaloyl chloride was prepared by the action of phosphorus pentachloride on pure isophthalic acid, obtained by permanganate oxidation of *m*-xylene (Eastman Kodak Co. "white label").[14] The product was purified by fractionation at reduced pressure followed by two recrystallizations from dry petroleum ether; m. p. 43.6°.

2,2′-Diphenoyl chloride was prepared in good yields from the corresponding acid by treatment with phosphorus

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(5) J. H. Hildebrand, "Solubility of Non-Electrolytes," Reinbold Publishing Corporation, New York, N. Y., 1936.

(6) R. Hill and E. E. Walker, *J. Polymer Sci.*, **3**, 609 (1948).

(7) See for example, W. H. Carothers and G. L. Dorough, THIS JOURNAL, **52**, 711 (1930); W. H. Carothers, J. A. Arvin and G. L. Dorough, *ibid.*, **52**, 3293 (1930); E. L. Lovell and H. Hibbert, *ibid.*, **62**, 230 (1940).

(8) Copolymeric character may also be introduced by N-alkylation of polyamides: see B. S. Biggs, C. J. Frosch and R. H. Erickson, *Ind. Eng. Chem.*, **38**, 1016 (1946); E. L. Wittbecker, R. C. Houtz and W. W. Watkins, *ibid.*, **40**, 875 (1948).

(9) W. E. Catlin, E. P. Czerwin and R. H. Wiley, *J. Polymer Sci.*, **2**, 412 (1947); see also, K. Hosino, *Bull. Chem. Soc.* (*Japan*), **19**, 156 (1944).

(10) For a preliminary report on the present investigation see *J. Chem. Phys.*, **15**, 685 (1947).

(11) H. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937, p. 99.

(12) We are indebted to Dr. L. E. Schniepp of the Northern Regional Research Laboratory for furnishing us with the sample of 1,5-pentanediol.

(13) H. Adkins and H. I. Cramer, THIS JOURNAL, **52**, 4349 (1930).

(14) M. E. Smith, *ibid.*, **43**, 1920 (1921).

pentachloride. It was recrystallized from hexane; m. p. 90–91°. The diphenic acid was prepared by the method of Atkinson and Lawler.[15] Decamethylene diamine was prepared by the method of Biggs and Bishop.[16] The hexamethylenediamine was prepared by catalytic reduction of adiponitrile. The various amine salts were prepared essentially as described recently.[17] The resorcinol, hydroquinone, benzoyl chloride and cyclohexanol used in minor amounts in the preparation of various polymers were of standard purity.

Preparation of Polymers.—Polyesters and copolyesters used in all experiments, except one series on the influence of molecular chain length on T_m, were prepared by co-reaction of glycol(s) and acid chloride(s).[18] The acid chloride, or mixture of acid chlorides, was introduced from a Lunge weighing pipet into a polymerization tube about 2 cm. in diameter and 30 cm. in length sealed at the lower end and equipped with a side arm near the open upper end. The tube was immersed in cold water and the glycol or mixture of glycols (and any other ingredients) was added. A small stoichiometric excess, usually about 1%, of the glycol(s) was used. In order to assure a random sequence of the repeating units in the polymer chains, the contents of the tube were thoroughly mixed by a slow stream of pure dry nitrogen admitted through a glass pipet type viscometer[19] inserted through the upper end of the polymerization tube. The temperature was gradually raised to 110°, where evolution of hydrogen chloride became vigorous. After about fifteen minutes, the temperature was raised to 201° where it was maintained for two hours during which period the slow stream of nitrogen was continued for the dual purpose of providing stirring and facilitating removal of the hydrogen chloride by-product. The viscosity rose rapidly during the heating period at the higher temperature, but usually approached constancy at the end of two hours; detectable evolution of hydrogen chloride likewise ceased by the end of this time. Viscosities were obtained as previously described[19] from the time required to fill the viscometer at a measured reduction of the pressure within the viscometer.

Polyamides and copolyamides were prepared by heating the diamine–dibasic acid salts, mixed in appropriate proportions, in an inert atmosphere at 218–241° until the viscosity reached 200 poises or more.[17] In contrast to the copolyesters, the copolyamides when cooled in bulk from the melt exhibited indefinite and poorly reproducible melting temperatures. This difficulty was overcome by casting specimens for melting point determination from dilute (less than 2%) solutions of the copolyamide in formic acid and evaporating the solvent. Melting temperatures of specimens so prepared were reasonably sharp and reproducible.

Volume–Temperature Measurements.—Changes in volume with temperature through the melting range were determined with conventional dilatometers[20] using mercury as the confining liquid, the level in the calibrated capillary being read with a cathetometer. The polymer sample (about 3–4 g.) was heated in vacuum at 109° until free of bubbles, then cooled, accurately weighed and inserted in the bulb of the dilatometer. The dilatometer was sealed and then maintained for twenty-four hours at high vacuum before the mercury was added without breaking the vacuum. The quantity of mercury in the dilatometer was determined by weighing. The volume was measured at successively increasing temperatures, at intervals, usually of one degree, the temperature being maintained constant within ±0.05° in an oil bath until apparent equilibrium was reached at each step. The temperatures were easily maintained for long periods of time by employing a modified thyratron electron relay of the type described by Weissberger.[21] Absolute specific volumes of the polymers were not obtainable from the dilatometer measurements alone since the volume of the dilatometer was not known. Values for the two pure polyesters subjected to volume–temperature measurements were taken from the values given in the literature,[19] and that of the copolyester included in this phase of the investigation was measured in a pipet pycnometer in the manner previously described.[19]

Determination of Melting Temperature.—While the equilibrium melting temperature is most accurately located from the dilatometric measurements, these are intolerably time consuming for extensive application. Observation of the temperature at which depolarization of plane polarized light passed through the specimen vanishes provides a sensitive means for determining disappearance of crystallinity. Reinhardt[22] applied this method in the observation of melting in polyvinylidene chloride copolymers, and Bunn and Alcock[23] have noted that the total disappearance of spherulitic structure in polyethylene, observed between crossed Nicols with a microscope, occurs at a consistently reproducible temperature, provided the rate of heating is sufficiently slow to assure thermal equilibrium.

We have employed a micro-melting point apparatus[10] consisting of an electrically heated aluminum specimen holder mounted on the stage of a low power (× 50) microscope. The disk shaped holder (3 cm. × 6 cm. diameter) possesses a circular indentation 2 cm. in diameter at the center in which the sample may be placed between two microscope cover glasses. Light was transmitted through a hole 2 mm. in diameter extending from the indentation through the disk. A circular aluminum plate with a hole 2 cm. in diameter at its center covered the heated disk and sample for the purpose of providing temperature uniformity. The apparatus was shielded from the microscope stage with asbestos. The temperature, controlled by varying the voltage input to the heating element within the disk, was read on a thermometer inserted horizontally in a well in the side of the heated disk. A Polaroid sheet was placed in the light beam below the stage of the microscope and another, at right angles to the former, was placed in the microscope objective. Semi-crystalline specimens appear bright in a dark field under these conditions. The temperature at which this brilliance disappears is taken as T_m. The thermometer was carefully calibrated, and the melting points of various pure organic compounds determined by this method were found to agree within one degree with those obtained in capillary tubes. If the heating rate is sufficiently slow, *i. e.*, not greater than one degree per minute, the observed melting temperatures of polymers generally are quite sharply definable and reproducible within a range of about 2° on different specimens (in finely divided form, *e. g.*, powder, film or small shaving) from the same sample. The melting temperatures are somewhat less distinct for copolymers containing large proportions of the co-ingredient.

Melting points of polymer–diluent mixtures were determined in small cells consisting of two microscope cover glasses separated by a 1-mm. iron washer, the lower cover glass being cemented with sodium silicate to the washer. The polymer and diluent in the desired proportion were mixed thoroughly at a temperature about 50° above T_m for the polymer. After gradually cooling the mixture, a small portion was placed within the cell and the top cover glass was set in place. The cell and contents were placed in the hot stage of the micro-melting point apparatus and the above-described procedure was applied.

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(15) E. R. Atkinson and H. J. Lawler, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 222.

(16) B. S. Biggs and W. S. Bishop, "Organic Syntheses," Vol. 27, John Wiley and Sons, New York, N. Y., 1947, p. 18.

(17) D. D. Coffman, G. J. Berchet, W. R. Peterson and E. W. Spanagel, *J. Polymer Sci.*, **2**, 306 (1947).

(18) In a few cases the polymerization was conducted in an inert solvent.

(19) P. J. Flory, THIS JOURNAL, **62**, 1057 (1940).

(20) N. Bekkedahl, *J. Research National Bur. Standards*, **43**, 145 (1949).

(21) A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945.

(22) R. C. Reinhardt, *Ind. Eng. Chem.*, **35**, 422 (1943).

(23) C. W. Bunn and T. C. Alcock, *Trans. Faraday Soc.*, **41**, 317 (1945).

Results

The Melting Process.—The results of dilatometric measurements on decamethylene sebacate are shown in Fig. 1. In Fig. 2 corresponding results for decamethylene adipate and the 70:30 copolymer of the latter with decamethylene isophthalate are shown. Each point represents the specific volume reached after no further change with time could be detected at the specified temperature. The temperature was then raised to that for the next higher point, etc. At temperatures immediately preceding T_m two or three days were required before the volume became constant; at other temperatures, apparent equilibrium was rapidly reached. Pre-melting of the pure polymers sets in appreciably at least 10° below T_m, but three-fourths of the melting appears to occur within 2° of T_m; the rate of disappearance of crystallinity with temperature increases continuously up to T_m. These characteristics of the transformation, and in particular the narrow temperature range over which most of the melting occurs, are in full accord with the predictions of theory[4] for the melting of semi-crystalline high polymers under equilibrium conditions.

The above melting behavior for linear polyesters is in sharp contrast with that for polyethylene. Hunter and Oakes[24] have shown by means of volume–temperature measurements, and Raine, Richards and Ryder[25] from heat capacity measurements, that fusion of the crystalline portions of polyethylene occurs over a range of at least 50° and three-fourths of the melting occurs over a range of 20–25°. This broad melting range is indicative of heterogeneity in constitution; it is suggestive of a copolymeric substance. The nonlinearity of polyethylene which gives rise to an excessive proportion of methyl groups over that to be expected for a high molecular weight linear polymer is well known,[26] and it is possible that exclusion of branched units and terminal methyl groups from the crystallites is responsible for the broad melting range observed for polythene, just as the co-ingredient of a copolymer broadens its melting range. Whereas Hunter and Oakes[24] succeeded in duplicating the same volume–temperature curve on cooling polyethylene very slowly, the polyesters invariably supercooled several degrees before crystallization set in.

Further work now in progress has shown that the melting behavior of the polyester depends on the previous thermal history. Thus, when molten decamethylene sebacate was rapidly cooled to 55° until crystallization commenced and then warmed to 75°, the crystals formed at 55° melted entirely and for a period the polymer persisted in the supercooled totally liquid condition at 75°. This observation is akin to that of Bekkedahl and Wood[27] on rubber, the melting temperature of which depends directly on the temperature at which crystallization took place. When the sample is strongly supercooled, imperfect arrangements of chains may form correspondingly imperfect crystallites which nevertheless are stable at this temperature. Owing to their imperfections, however, they become unstable relative to the liquid state at a temperature significantly below T_m. In the case of the polyesters gradual cooling of the molten polymer leads to a semi-crystalline arrangement in which these effects are no greater than a degree or two, and they are further minimized, insofar as the determination of T_m is concerned, by the long times (one day or more) at which the sample was maintained at each temperature in the vicinity of T_m.

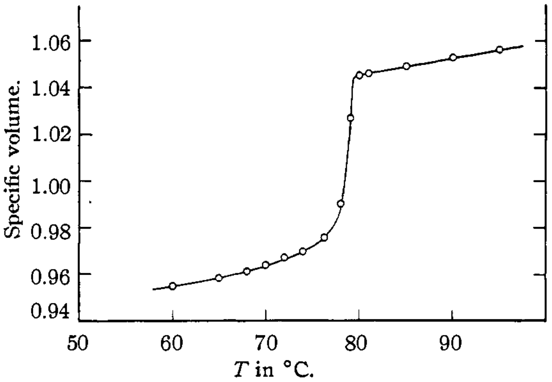

Fig. 1.—Specific volume *vs.* temperature for decamethylene sebacate.

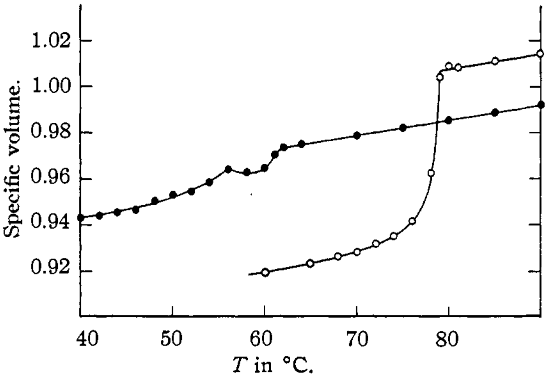

Fig. 2.—Specific volume *vs.* temperature for decamethylene adipate (○) and for a copolyester (●) consisting of 70 mole per cent. of decamethylene adipate units with 30 mole per cent. of decamethylene isophthalate.

The 70:30 copolyester (Fig. 2) melts over a much broader range, as is to be expected. There is an indication of recrystallization between 56 and 60°; crystallinity appears to have nearly disappeared at 56°, but a decrease in volume takes

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(24) E. Hunter and W. G. Oakes, *Trans. Faraday Soc.*, **41**, 49 (1945).

(25) H. C. Raine, R. B. Richards and H. Ryder, *ibid.*, **41**, 56 (1945).

(26) H. W. Thompson and P. Torkington, *Proc. Roy. Soc.* (*London*), **A184**, 3 (1945).

(27) N. Bekkedahl and L. A. Wood, *J. Chem. Phys.*, **9**, 193 (1941); see, also, "Advances in Colloid Science," Vol. II, edited by H. Mark and G. S. Whitby, Interscience Publishers, Inc., New York N. Y., 1946, Chapter 2 by L. A. Wood.

place on raising the temperature, which may be due to the formation of more perfect crystalline arrangements. A total specific volume change of about 0.015 is attributable to melting over the temperature range investigated compared with about 0.075 for decamethylene adipate. The coefficients of expansion of the polyesters and the copolyester above their melting points agree with those previously reported.[19]

TABLE I

COMPARISON OF MELTING TEMPERATURES OBTAINED BY THE MICRO MELTING POINT METHOD WITH THOSE DEDUCED DILATOMETRICALLY

Polymer	Viscosity at 201° in poises	T_m micro method	T_m, from specific volume
Decamethylene sebacate	645	82.5–84.5	80
Decamethylene adipate	215	80–82	79.5
Decamethylene adipate (70): Decamethylene isophthalate (30)	470	57.5–58.5	61

Melting temperatures obtained with the micro-melting point apparatus are compared in Table I with those taken from the volume–temperature plots of Figs. 1 and 2. In this table, as in the others which follow, the variation in the temperature at which disappearance of depolarization was observed on different specimens is indicated by the temperature range given. For the two polymers the melting temperatures observed by the micro method tend to be somewhat too high; the reverse is true for the copolymer. Poor thermal conductivity may account for a part of the discrepancy for the polymers, although no significant effect of diminishing the rate of heating was observed. The low values obtained by this method when applied to copolymers doubtless is due to non-equilibrium crystallization not unlike that occurring when a molten polymer is rapidly cooled, as discussed above. It must be concluded that the micro method yields values for T_m which are approximate only. Although by no means as precise as the dilatometric method when applied as above, the micro method nevertheless is sufficiently accurate for a first attempt at the quantitative delineation of the effects of composition and molecular weight on the melting temperature.[28]

Copolyesters.—Melting temperatures determined by the micro method are given in Tables II to VI for various copolyesters prepared by reacting the indicated mixtures of glycols with a given dibasic acid chloride, or by treating a given glycol with the indicated mixture of dibasic acid chlorides. The repeating structural unit consists in each case of one glycol and one dibasic acid residue. In the former type of copolyester (Tables II, IV and VI) the portion of a polymer chain consisting of the principal glycol residue followed by the acid residue is regarded as the "A" unit, and a co-ingredient glycol and acid residue as the "B" unit. Thus, the mole fraction X_A of A units in these polymers is equal to the molar ratio of the

TABLE II

DECAMETHYLENE–*cis*-1,4-CYCLOHEXAMETHYLENE ADIPATE COPOLYESTERS

X_A = Mole fraction of decamethylene adipate	Viscosity in poises at 218°	T_m, °C.
0.95	450	80–81
.90	380	72.5–74.5
.85	360	70–72.5
.80	310	66.5–67.5
.75	135	63.5–65
.70	230	63.5–65
.60	360	67–71

TABLE III

DECAMETHYLENE ISOPHTHALATE–ADIPATE COPOLYESTERS

X_A = mole fraction of decamethylene adipate	Viscosity in poises at 218°	T_m, °C.
0.95	100	76–77.5
.90	420	72.5–74.5
.85	170	69.5–70.5
.80	600	64.5–65.5
.70	1100	57.5–58.5
.60	1000	49–52

TABLE IV

DECAMETHYLENE–*cis*-1,4-CYCLOHEXAMETHYLENE SEBACATE COPOLYESTERS

X_A = mole fraction of decamethylene sebacate	Viscosity in poises at 218°	T_m, °C.
0.90	185	80–81
.80	240	72–75
.70	...	68–70

TABLE V

DECAMETHYLENE ISOPHTHALATE–SEBACATE COPOLYESTERS

X_A = mole fraction of decamethylene sebacate	Viscosity in poises at 218°	T_m, °C.
0.90	...	77–79
.80	290	70–73
.70	190	63–65
.60	...	58–59

TABLE VI

DECAMETHYLENE–PENTAMETHYLENE ADIPATE COPOLYESTERS

X_A = mole fraction of decamethylene adipate	T_m, °C.	T_m, °C. calcd.	ΔT, °C.
0.90	78–79	74.5	+ 4.0
.80	73.5–75.5	66	+ 8.5
.75	70.5–71	62	+ 9.0
.70	68.5–70.5	58	+11.5
.60	63.5–65	50	+14.0

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(28) Mention should be made of the observation that redetermination of T_m on a specimen previously allowed to cool from the molten condition in the micro-melting point apparatus almost invariably gives lower values. This is believed to result from non-equilibrium crystallization which takes place as noted above when the molten sample is allowed to cool rapidly, as when the heating current in the micro melting point apparatus is shut off.

principal glycol to the total glycol. The mole fraction of "A" units in copolyesters formed from a given glycol and a mixture of two acid chlorides is correspondingly given by the molar ratio of the principal acid chloride to the total acid chloride.

The sets of data from Tables II and III for the two series of decamethylene adipate copolymers are shown in Fig. 3, where T_m is plotted against the composition. The approximate uncertainty in T_m is indicated by the size of the point in each case. The dependence of T_m on X_A is the same within experimental error for the two series (*i. e.*, regardless of whether the co-unit is *cis*-1,4-cyclohexamethylene adipate or decamethylene isophthalate) from $X_A = 1.0$ to 0.75. As X_A is further decreased the copolymers with cyclohexamethylene adipate indicate a eutectic composition between $X_A = 0.75$ and 0.70. Decamethylene isophthalate is non-crystalline at room temperature, hence no eutectic is observed for the other copolymer system within the composition range investigated.

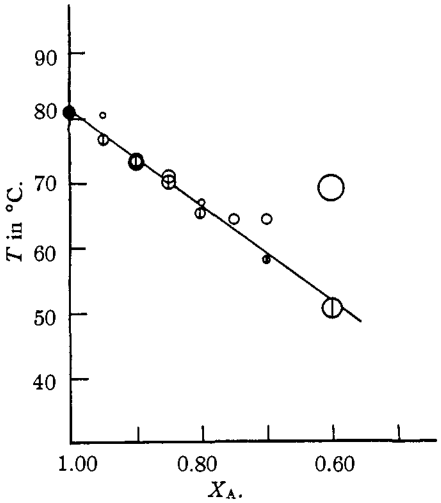

Fig. 3.—Melting temperature T_m *vs.* mole fraction X_A of decamethylene adipate units in copolymers with decamethylene isophthalate (⦶) or *cis*-1,4-cyclohexamethylene adipate (O) (data from Tables II and III).

In Fig. 4 the same data are plotted as $1/T_m$ *vs.* ln X_A in accordance with equation (1), and in Fig. 5 the results given in Tables IV and V for the analogous copolyester systems in which decamethylene sebacate is the principal ingredient are similarly plotted. Heats of fusion per structural unit, calculated by means of Eq. (1) from the slopes of the straight lines drawn in Figs. 4 and 5, are given in Table X.

The four sets of results discussed above suggest that the depression in T_m caused by introduction of a given mole fraction of a co-ingredient is independent of the co-ingredient used, so long as a eutectic composition is not exceeded. Numerous exceptions to this rule have been found, however. Data for one such copolymer series are shown in Table VI. The "calculated" T_m values are those obtained from the line drawn in Fig. 4 and the "ΔT's" represent differences between T_m observed and T_m "calculated" in this manner.

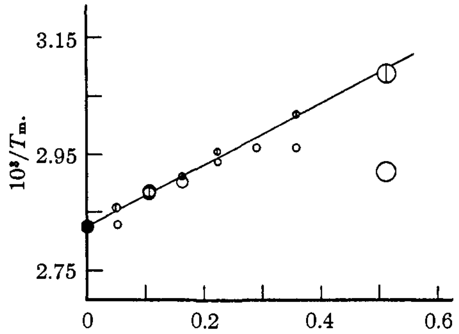

Fig. 4.—Reciprocal melting temperature T_m of decamethylene adipate copolyesters as a function of ln X_A: co-ingredients, decamethylene isophthalate (⦶) and *cis*-1,4-cyclohexamethylene adipate (O) (data from Tables II and III).

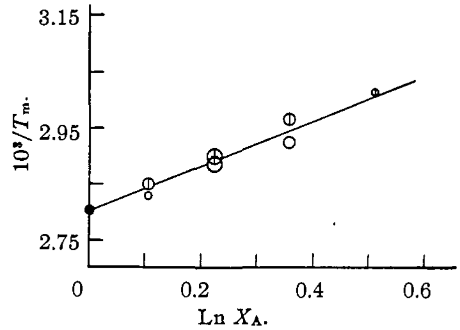

Fig. 5.—$1/T_m$ *vs.* ln X_A for decamethylene sebacate copolyesters, co-ingredients: decamethylene isophthalate (⦶) and *cis*-1,4-cyclohexamethylene sebacate (O) (data from Tables IV and V).

The T_m values for various decamethylene adipate copolyesters in which $X_A = 0.80$ are assembled in Table VII. Discrepancies between the observed T_m's and that given by the line of

TABLE VII

COPOLYESTERS CONTAINING 80 MOLE PER CENT. DECAMETHYLENE ADIPATE (X_A = 0.8)

Co-ingredient	T_m, °C., obs.	ΔT, °C.[a]
cis-1,4-Cyclohexamethylene adipate	66.5–67.5	+ 1.0
Resorcinol adipate	64–65	− 1.5
Hydroquinone adipate	77–82	+13.5
Tetramethylene adipate	73.5–75.5	+ 8.5
Diethylene adipate	72.5–73	+ 7.0
Pentamethylene adipate	73.5–75.5	+ 8.5
Decamethylene isophthalate	64.5–65.5	− 1.0
Decamethylene 2,2′-diphenoate	61.5–63.5	− 3.5
Decamethylene sebacate	72–75	+ 7.5

[a] ΔT represents the mean difference between the T_m observed and 66°, the "calculated" value for T_m at X_A = 0.80.

Fig. 4, namely, 66°, are recorded in the last column. It will be observed that when the co-ingredient is another polymethylene glycol (including also diethylene glycol) or another polymethylene dibasic acid the depression in T_m is invariably less (*i. e.*, ΔT is positive) than the "calculated" depression by an amount substantially beyond the experimental uncertainty. This anomaly is believed to arise from the tolerance of the A crystallite for the B structural unit, the crystallites which form in these copolymers being analogous to solid solutions. It is to be noted, however, that the crystalline zones do not accept B units in place of A units indiscriminately in any of the examples investigated, for in no case is T_m unaffected by the presence of B units. The aggregate interactions between the polymethylene chains in these polyesters are known to dominate the inter-chain polar interactions between ester groups.[29,30] Consequently, some of the foreign repeating units may occur within crystallites in spite of the inability of their ester groups to locate in the polar layers spaced at intervals characteristic of the A repeating unit. The resulting imperfect crystalline regions exhibit lower melting points than the perfect crystallites formed from the pure A polymer, but they nevertheless represent a condition of greater thermodynamic stability than would result from the more limited degree of crystallinity attainable exclusively from the small proportion of sequences of A units in the copolymer. Melting points therefore are lower than for the pure polymer though higher than those for the copolymer prepared from bulkier co-ingredients.[31]

Melting points for the 80:20 decamethylene adipate copolymers containing the bulkier cyclic co-ingredients are in close agreement (Table VII) with the exception of the copolymer with hydroquinone. The melting point of hydroquinone adipate is very high, and unquoted experiments indicated that the eutectic for this system lies at more than 80 mole per cent. of decamethylene adipate. The small depression observed in this case should not, therefore, be attributed to the formation of mixed crystallites.

Copolyamides.—Investigations on the melting temperatures of copolyamides have been confined to two series. Decamethylene sebacamide was the principle ingredient in one of these, and decamethylene adipamide in the other The results given in Tables VIII and IX, respectively, are shown graphically in Fig. 6 where each point includes the T_m values observed for the several copolyamides having the same molar compositions of the principal ingredient. According to the results presented in Tables VIII and IX, the melting point depression is very nearly independent of the particular co-ingredient used in all cases. The calculated values for T_m given in the last columns of Tables VIII and IX have been taken from the straight lines drawn through the two sets of points in Fig. 6. Heats of fusion, calcu-

TABLE VIII

COPOLYAMIDES OF HEXAMETHYLENE SEBACAMIDE

Co-ingredient[a]	X_A	T_m, °C., obs.	T_m, °C. calcd.
	1.0	225.5–226	...
10-10	0.9	218.5–221	220
6-Isophthalamide	.9	219–221.5	220
10-10	.8	209–212.5	212
6-Isophthalamide	.8	210–214	212
6-6	.8	211.5–214	212
10-10	.7	202–204	203.5
6-Isophthalamide	.7	201–206	203.5

[a] The numerals refer to the number of carbon atoms in the polymethylenediamine or dibasic acid, the number given first referring to the former. Thus, 10-10 denotes decamethylene sebacamide.

TABLE IX

COPOLYAMIDES OF DECAMETHYLENE SEBACAMIDE

Co-ingredient	X_A	T_m °C. obs.	T_m °C. calcd.
	1.0	208.5–210	...
10-Terephthalamide	.9	203.5–205.5	203.5
6-10	.9	202–204.5	203.5
6-10	.8	195–200	197
10-6	.8	193.5–196.5	197
10-Isophthalamide	.8	194–198	197
Piperazine-10	.8	195–199	197
6-6	.8	196–200.5	197
6-10	.7	186–191	189.5
6-10	.6	179–183	181.5

TABLE X

HEATS OF FUSION OF POLYESTERS AND POLYAMIDES

Polymer	h_u From copolymer data, cal./repeating unit	—Heat of fusion in cal./g.— From copolymer data	From influence of chain length	From influence of dilution
Decamethylene adipate	3800	13.4	37.5	
Decamethylene sebacate	4700	13.8		36[a]
Decamethylene sebacamide	7800	23.1		
Hexamethylene sebacamide	7300	25.9		

[a] The figure given is the mean for the closely agreeing values obtained from solutions in diethyl sebacate and benzophenone. The result deduced from the melting points of the diethyl succinate solutions is much higher, 55 cal./g.

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[29] W. O. Baker in "Advancing Fronts in Chemistry, Vol. I," edited by S. B. Twiss, Reinhold Publishing Corp., New York, N. Y., 1945, Chapter 8.

[30] W. A. Yager and W. O. Baker, THIS JOURNAL, **64**, 2164 (1942).

[31] The copolyester prepared from ethylene glycol and an equimolar mixture of the 10-, 11- and 12-carbon polymethylene dibasic acids, according to X-ray results obtained by Fuller, THIS JOURNAL, **70**, 421 (1948), forms a compromise lattice differing from that of any one of the constituent units alone. Bunn, *Nature*, **161**, 929 (1948), has similarly reconciled the crystallinity of polyvinyl alcohol with the presence of a mixture of *d*- and *l*-HC_2-CHOH- units by postulating a mixed crystal lattice which is consistent with the observed X-ray diffraction pattern. While neither the results given above nor our interpretation of them is inconsistent with the formation of a compromise lattice unlike the lattice for the pure A polymer, the formation of an imperfect lattice closely resembling the A-type lattice seems plausible for minor proportions of the co-ingredient.

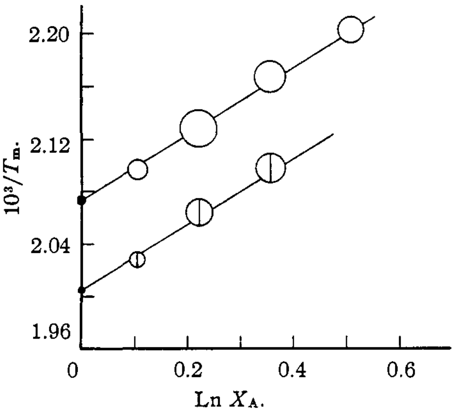

Fig. 6.—$1/T_m$ *vs.* ln X_A for copolyamides in which the principal ingredient is decamethylene sebacamide (O) or hexamethylene sebacamide (⦶). Each point represents combined results for various co-ingredients (data from Tables VIII and IX).

lated from the slopes of these lines and recorded in Table X, are nearly twice those for the polyesters.

The greater heats of fusion of the polyamides are to be expected in view of the high polarity and the hydrogen bonding capacity of the amide linkage. Baker[29] and Fuller[32] have shown that, in contrast to the aliphatic polyesters, interaction between the more polar linkages of the corresponding polyamides dominates interaction between the polymethylene chains. Consequently, the polyamides supercool more easily as found by these authors, and long relaxation times are observed in dielectric measurements.[33] For the purposes of our experiments it has been necessary to prepare the samples by deposition from a solvent (formic acid, see above) in order to obtain reproducible melting points which appear to be reasonably near equilibrium values.

Failure to observe evidences of the formation of mixed crystals, even in the case of an homologous aliphatic co-ingredient, provides further evidence for the dominance of polar layer interaction in polyamides as set forth by Baker and Fuller.[32] Separate crystallization of the two ingredients in aliphatic copolyamides is also indicated by Baker and Fuller's[32] X-ray measurements on the layer line spacing as a function of copolymer composition. Abrupt changes were observed to occur in two cases (6-6 with 6-10 and 6-6 with 10-6) at intermediate compositions, which may be presumed to correspond to the eutectics. At all other compositions the spacing approximates that of the component present in excess of the eutectic composition. In other cases (10-6 with 10-10, 6-6 with 10-10, and 6-6 with 9-9) more complex changes in the layer identity period were observed to occur throughout the composition range. These latter observations indicate mixed crystal formation as discussed by Baker and Fuller. Results such as these do not necessarily conflict with the conclusions drawn from the present melting point studies, inasmuch as the X-ray diffractions were carried out at temperatures far below the melting temperature. Our investigations have been concerned only with the crystalline order of maximum stability which alone survives at temperatures close to T_m. We have found further that the annealing methods employed by Baker and Fuller are inadequate for achieving reproducible melting points, and it is quite possible that some of their specimens possessed types of order not present in our samples. That different types of order may be obtained through different thermal (and mechanical) treatments applied to the same polymer has been abundantly demonstrated by Baker and Fuller.[34]

The Influence of Molecular Weight on Melting Temperature.—A series of polyester samples varying in molecular weight was obtained by condensing equimolar proportions of decamethylene glycol and adipic acid at 110° in the presence of a small amount of *p*-toluenesulfonic acid catalyst.[35] Samples were removed at suitable intervals, and their average molecular weights were calculated from concurrently measured melt viscosities using the previously established empirical relationship.[19] In Fig. 7 reciprocal melting temperatures determined by the micro method are plotted, as prescribed by Equation (2), against the reciprocal of the number average degree of polymerization $\bar{x}_n$. Here $\bar{x}_n$ represents the average number of repeating units $-O(CH_2)_{10}O-CO(CH_2)_4CO-$, as is required by the theory leading to equation (2).[36] A straight line has been drawn through the points, despite a significant deviation from linearity for the highest molecular weight samples (*i. e.*, near

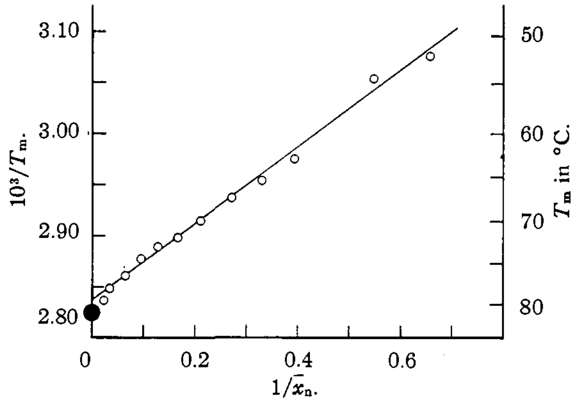

Fig. 7.—$1/T_m$ *vs.* the reciprocal of the number average number $\bar{x}_n$ of repeating units in decamethylene adipate polymers terminated with hydroxyl and carboxyl groups.

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

[33] W. O. Baker and W. A. Yager, *ibid.*, **64**, 2171 (1942).

[34] W. O. Baker and C. S. Fuller, *ibid.*, **65**, 1120 (1943).

[35] P. J. Flory, *ibid.*, **61**, 3334 (1939).

[36] In previous publications the symbol x_n has been used to represent the number of *structural units* in condensation polymers. In those of the glycol-dibasic acid type each *repeating unit* consists of two structural units. See THIS JOURNAL, **58**, 1877 (1936); also ref. 19.

the origin). The heat of fusion calculated from the slope of the line is 10,700 cal. per structural unit, a value much higher than that deduced from the results on copolyesters (see Table X).

It will be noted that the form of the dependence of T_m on $\bar{x}_n$ shown in Fig. 7 is based to a large extent on samples of very low average molecular weight, the range extending somewhat below an average of two repeating units. The significance of results in this range might seem to be highly questionable. However, the theory[4] predicts that the most stable crystallites will be formed from the highest polymer molecules present in the sample. Although T_m should depend on the number average, $\bar{x}_n$ (for the random type of distribution occurring in condensation polymers), the last crystals to disappear at the melting temperature should be composed of polymers many times $\bar{x}_n$ in length, therefore.

Equation (2) has been derived on the assumption that terminal groups of the polymer chain will not occur within the crystallites. Although certain theoretical considerations support this assumption in part,[4] experimental verification is clearly desirable. To this end, low molecular weight decamethylene adipate polymers having bulky terminal groups were prepared and their melting temperatures determined. One such series, results for which are shown in Fig. 8, was prepared by treating decamethylene glycol with an equivalent amount of a mixture of adipyl chloride and benzoyl chloride in proportions chosen to give the desired molecular weight at completion of the condensation. Molecules of the polymer so produced are expressed by the formula

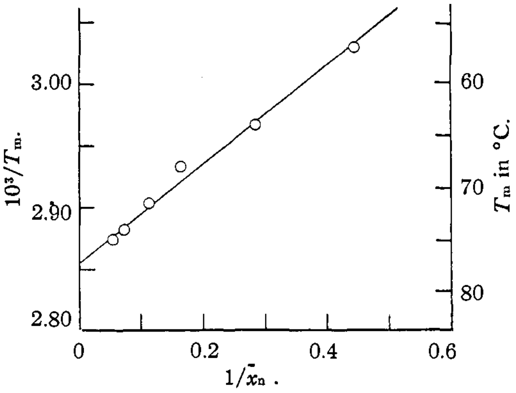

Fig. 8.—$1/T_m$ vs. $1/\bar{x}_n$ for decamethylene adipates terminated with benzoate end-groups.

$$C_6H_5CO—[O(CH_2)_{10}O—CO(CH_2)_4CO—]_xO(CH_2)_{10}O—COC_6H_5$$

The number average value of x, or $\bar{x}_n$, required in equation (2) is given by twice the ratio of adipate to benzoate radicals in the system. A series of decamethylene adipate polymers terminated with α-naphthoate groups was similarly prepared, and another terminated with cyclohexyl groups was obtained by treating mixtures of decamethylene glycol and cyclohexanol with adipyl chloride. Results for these two series are shown in Figs. 9 and 10. Slopes of the straight lines in Figs. 8, 9 and 10 lead to heats of fusion per structural unit of 10,600, 9,500 and 11,300 cal., respectively. Within experimental error, all of these agree with the value obtained for the polyesters terminated by hydroxyl and carboxyl groups (Fig. 7). As it is inconceivable that the bulky end groups could enter the crystallites, concurrence of the results for the above four series substantiates the previous tentative conclusion that terminal units, regardless of size, generally will not occur within crystallites.

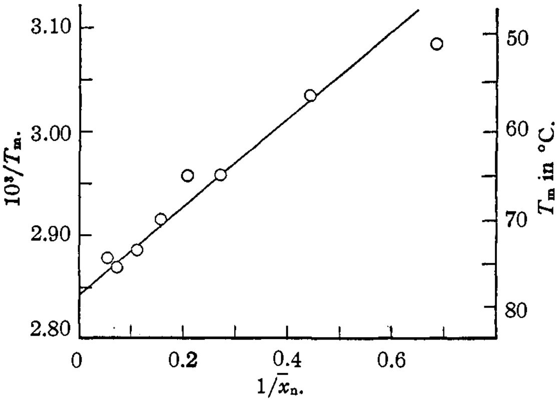

Fig. 9.—$1/T_m$ vs. $1/\bar{x}_n$ for decamethylene adipates terminated with α-naphthoate end-groups.

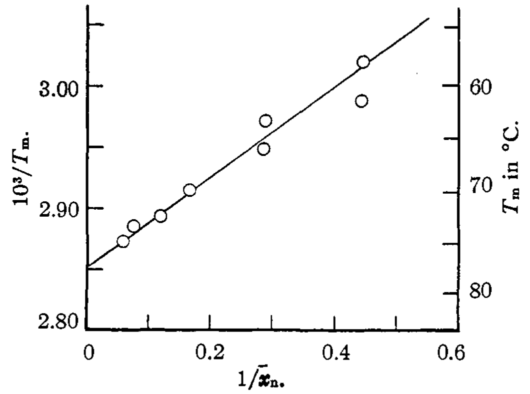

Fig. 10.—$1/T_m$ vs. $1/\bar{x}_n$ for decamethylene adipates terminated with cyclohexyl end-groups.

The large discrepancy between the heats of fusion estimated from the dependences of T_m on copolymer composition and on average chain length represents the most serious indictment of the theoretical relationships put to test by the present experiments. It is possible, in analogy with numerous results on other long chain compounds, that different crystalline forms may be involved, the one stable only at temperatures near the melting temperature T_m^0 although capable of persisting at lower temperatures, and the other, having a higher heat of fusion, becoming the stable form a few degrees below the melting point. The fact that the lines drawn in Figs. 7, 8, 9 and 10 extrapolate to limiting temperatures for $\bar{x}_n = \infty$ which are several degrees below observed T_m^0 lends some support to the view that the lower melting form is involved in these experiments. Further experiments on other polymer systems clearly are needed to clarify the source of this discrepancy.

Influence of Diluents on Melting Temperature.—Results of a preliminary nature on the melting temperature for decamethylene sebacates in three diluents, diethyl succinate, diethyl sebacate and benzophenone are shown in Fig. 11 where $1/T_m$ is plotted against the volume fraction of diluent. The data are satisfactorily represented by straight lines, which would suggest that the heat of mixing term in Equation (3) is small enough to be neglected. The slopes of the straight lines therefore should be equal to $(R/h_u)(z/z_s)$ according to this equation, where z/z_s is the ratio of the molar volumes of the repeating unit and the diluent. Letting h_f represent the heat of fusion per gram, the slope can be equated alternatively to $R/\rho V_s h_f$ where ρ is the density of the polymer in liquid state and V_s is the molar volume of the diluent. Assuming an estimated value of $\rho = 0.99$[19] at 25° and employing molar volumes of the diluents at the same temperature, the heats of fusion calculated in this manner from the results obtained with the three diluents, diethyl succinate, diethyl sebacate and benzophenone, are 55, 37 and 34.5 cal. per g., respectively. (The difference between the slopes for the diethyl sebacate and benzophenone sets of data is accounted for by the difference in their molar volumes.) The cause of the divergence of the heat of fusion calculated from the results obtained using diethyl succinate is not clear; occurrence of diethyl succinate in the crystal lattice would afford a possible explanation.

The heats of fusion calculated from the effects of dilution with diethyl sebacate and with benzophenone are in good agreement with the heat of fusion deduced from the dependence of T_m on chain length (see Table X). It is to be noted that the lines drawn in Fig. 11 extrapolate to a temperature several degrees below the observed T_m^0 for the pure polymer. This discrepancy is like that observed in the study of the dependence of T_m on molecular weight, and it suggests that here also a low temperature stable crystalline form, differing from that encountered in the experiments on copolymers, may be involved.

Melting Behavior of Polyethylene–Diluent Mixtures.—Richards[37] has determined the melting points of mixtures of Polythene (commercial polyethylene) with various hydrocarbons. His results, interpolated to compositions consisting of equal parts of polyethylene and diluent, are given in Table XI. The calculated temperature depressions given in the last column have been deduced from Equation (3) taking $\mu = 0$ and assuming for the heat of fusion the same value,[25] 56 cal. per g., found for the higher n-paraffin hydrocarbons. Since the crystal structure of polyethylene corresponds to that of the low temperature stable form of the higher n-paraffin hydrocarbons, and since no change of crystal form is observed in polyethylene up to the melting point,[23] the use of this value for the heat of fusion is justified. The differences between the observed and calculated temperature depressions are scarcely beyond experimental error.

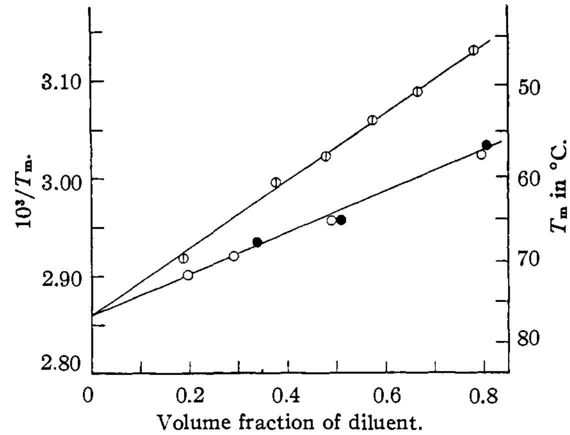

Fig. 11.—$1/T_m$ *vs.* the volume fraction of diluent for mixtures of decamethylene sebacate with diethyl succinate (○), diethyl sebacate (●) and benzophenone (⦶).

TABLE XI

MELTING POINT DEPRESSION[a] FOR 1:1 MIXTURES OF POLYETHYLENE WITH HYDROCARBON DILUENTS

Diluent	T_m interpolated for 1:1 mixture, °C.	$T_m^0 - T_m$	$T_m^0 - T_m$ calcd.[b]
None	109		
Heptane	92	17	21
Cetene-2	96	13	10
Paraffin wax, mol. wt. 350	101	8	7
Low molecular weight polyethylene mol. wt. 650	104	5	4

[a] Melting temperatures given in the second column are taken from the results shown in Fig. 3 of ref. 38. [b] According to Equation 3, $T_m^0 - T_m = RT_mT_m^0/\rho V_s h_f$. Taking $\rho = 0.85$[24] and $h_f = 56$ cal./g.[25] $T_m^0 - T_m = 3.0 \times 10^3/V_s$ from which the figures given in the last column have been calculated.

Summary and Conclusions

The disappearance of crystallinity with increase in temperature has been observed dilatometrically in two polyesters, decamethylene adipate and decamethylene sebacate, and in a 70:30 copolyester of the latter with decamethylene isophthalate. When temperature changes are scheduled so as to eliminate time dependent phenomena, more than half of the melting is confined to a range of only two degrees, and final disappear-

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[37] R. B. Richards, *Trans. Faraday Soc.*, **41**, 127 (1945).

ance of crystallinity occurs at a sharply defined temperature, T_m, in accordance with recent theory.[4] The copolymer acquires a much smaller degree of crystallinity even at lower temperatures and it melts over a much broader range. A well defined melting point for complete disappearance of crystallinity is nevertheless indicated.

Melting points T_m of polyesters varying in chain length, of polyester–diluent mixtures and of various copolyesters and copolyamides have been determined using a micro-melting point apparatus adapted to the observation of the temperature at which the specimen ceases to depolarize transmitted light. The melting points of the copolyamides and certain of the copolyesters depend on the mole fraction of the principal repeating unit in accordance with theory, and are independent of the nature of the co-ingredient. Copolyesters in which the co-ingredient differs from the principal unit only in the number of methylene groups separating the functional groups appear to form mixed crystals, for the melting point depressions are abnormally small in such cases.

As the chain length of decamethylene adipate is decreased $1/T_m$ increases linearly with the reciprocal of the number average number $\bar{x}_n$ of repeating units per molecule, as required by theory. This relationship is the same within experimental error regardless of whether the terminal groups are small (hydroxyl and carboxyl) or large (benzoate, α-naphthoate or cyclohexyl). The previous conclusion that terminal groups will tend to occur outside the crystallites appears to be well founded.

Diluents, including diethyl succinate, diethyl sebacate and benzoquinone, produce increases in $1/T_m$ for decamethylene sebacate which are proportional to the volume fraction of the diluent.

Theoretical relationships permit the calculation of net heats of fusion per gram of crystalline phase from the observed dependences of T_m on each of the above mentioned variables: copolymer composition, chain length and dilution. Values for decamethylene adipate and decamethylene sebacate calculated from the depression in T_m brought about by copolymerization are about 13 to 14 cal. per g. Much larger values are obtained from the dependence of T_m on chain length and from its dependence on dilution with monomeric substances. The source of this discrepancy has not been ascertained. Nevertheless, other results obtained justify further efforts to apply the statistically derived theories to semicrystalline polymers. The influence of foreign units, terminal groups and diluents on the melting of polymers appears to be closely analogous to the classical effects of impurities on solid-liquid equilibria in monomeric compounds.

AKRON, OHIO RECEIVED OCTOBER 31, 1949

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Exchange Reactions between Cyclohexyl Alkyl Bromides and Chloride Ion[1]

BY ALLEN L. SOLOMON[2] AND HENRY C. THOMAS[3]

The displacement of the halogen of an organic halide by a halide ion has been shown to proceed at a rate representable by a second order law.[4] The mechanism for an alkyl halide has been shown to be that of a Walden inversion.[5] Some investigation has been made of the reduction in reaction rate when the chain of an alkyl halide is branched near the reacting carbon. In this connection much attention has been given to neopentyl bromide.[6] Steric hindrance by alkyl groups to the approach of the halide ion has been offered as an explanation of this effect.[7]

Halide exchange reactions of cyclohexyl chloride and cyclohexyl bromide have been found to be extremely slow as compared to those of the alkyl halides.[3a,5a] The work reported here was undertaken to obtain more information on the effect of the cyclohexyl ring in such reactions. The rates of the reactions between chloride and each of cyclohexyl bromide, bromomethylcyclohexane, β-bromoethylcyclohexane, n-butyl bromide, and isobutyl bromide have been measured. In order to get results which should be nearly comparable as regards the effect of structure, the same solvent and similar concentration and temperature ranges were employed in each case. The solvent used was, by volume, nine parts of acetone and one part of water. Sugden and his co-workers[4b,8] have found several isotopic bromide exchange reactions to be second order in this solvent. We have assumed second order kinetics throughout. The reactions, except in the case of cyclohexyl bromide, are represented by the constants defined in the scheme

$$\mathrm{RBr} + \mathrm{Cl}^- \underset{k'}{\overset{k}{\rightleftharpoons}} \mathrm{RCl} + \mathrm{Br}^-$$

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(1) This paper is based on the dissertation presented in 1948 by Allen L. Solomon to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(4) (a) Conant and Hussey, THIS JOURNAL, **47**, 476 (1925); (b) LeRoux and Sugden, *J. Chem. Soc.*, 1279 (1939); (c) McKay, THIS JOURNAL, **65**, 702 (1943).

(5) Hughes, Juliusburger, Masterman, Topley and Weiss, *J. Chem. Soc.*, 1525 (1935).

(6) (a) Bartlett and Rosen, THIS JOURNAL, **64**, 543 (1942); (b) Dostrovsky and Hughes, *J. Chem. Soc.*, 161 (1946).

(7) (a) A. G. Evans, *Trans. Faraday Soc.*, **42**, 719 (1946); (b) Dostrovsky, Hughes and Ingold, *J. Chem. Soc.*, 173 (1946); (c) A. G. Evans, M. G. Evans and Polanyi, *ibid.*, 558 (1947).

(8) Elliott and Sugden, *J. Chem. Soc.*, 1836 (1939).