influence of hydrogen-bond or van der Waals forces to fit into a regular crystal lattice. Only if the clews are identical, as they are in globular proteins, can crystallization occur. Otherwise the structures are arrays of fibrous or helical structures in which some of the subunits are not identical. That is, these random copolymers can not form regular single crystals, although a block copolymer such as that studied by Lotz[30] can.

Conclusion

Polyhomomers having only R-equivalent groups form large, regular single crystals; so do polyhomomers having R-nonequivalent groups if they are truly stereoregular. As little as 1% allomer in a polymer can lead to the formation of small, irregular crystals. Single crystal formation can be used to judge the structural regularity of polymers.

Notes

Synthesis of Linear Aliphatic Polyesters

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In the course of studies[2–5] on structure–property relations in linear aliphatic polyesters, we have twice had occasion to synthesize[6] some of these polymers to as high molecular weights as feasible. Initially,[3] we relied on the direct esterification technique originally used by Carothers,[7] in which a dibasic acid is reacted with a glycol in bulk

$$n\mathrm{HOOC(CH_2)}_x\mathrm{COOH} + n\mathrm{HO(CH_2)}_y\mathrm{OH} \longrightarrow \mathrm{H[OCO(CH_2)}_x\mathrm{COO(CH_2)}_y]_n\mathrm{OH} + (n-1)\mathrm{H_2O}$$

However, polymers made in this way were purified only with difficulty and degraded to lower molecular weights with time.[8] We have therefore scouted three alternate syntheses.

1. acid chloride synthesis[9]

$$n\mathrm{ClOC(CH_2)}_x\mathrm{COCl} + n\mathrm{HO(CH_2)}_y\mathrm{OH} \longrightarrow \mathrm{Cl[OC(CH_2)}_x\mathrm{COO(CH_2)}_y]_n\mathrm{OH} + (n-1)\mathrm{HCl}$$

2. acid exchange[10]

$$n\mathrm{HOOC(CH_2)}_x\mathrm{COOH} + n\mathrm{CH_3COO(CH_2)}_y\mathrm{OCOCH_3} \longrightarrow \mathrm{H[OCO(CH_2)}_x\mathrm{COO(CH_2)}_y]_n\mathrm{OCOCH_3} + (n-1)\mathrm{CH_3COOH}$$

3. ester exchange[11]

$$n\mathrm{CH_3OCO(CH_2)}_x\mathrm{COOCH_3} + n\mathrm{HO(CH_2)}_y\mathrm{OH} \longrightarrow \mathrm{CH_3[OCO(CH_2)}_x\mathrm{COO(CH_2)}_y]_n\mathrm{OH} + (n-1)\mathrm{CH_3OH}$$

Although many other possibilities and variations (solution or interfacial polymerization) are possible, they were not tested.

The purpose of this paper is to describe the relative merits of each of the above-mentioned condensation techniques.

Experimental Section

Purification of Reagents. Chloroform (Fisher, reagent grade) was distilled from calcium sulfate through a 1-m vacuum column packed with glass helices. The center cut (about two-thirds of the total) was stored over degassed activated molecular sieves (Linde 4A). If to be used directly, it was degassed and twice vacuum distilled into a storage flask under a metal tap. This procedure does not remove ethanol from chloroform; to make this separation, chloroform purified as described was refluxed for 2 hr with 2% (by weight) of phenyl isocyanate (Eastman), and then 1 hr with 5% distilled water added. A water–chloroform mixture was distilled off and purified by distillation from calcium sulfate, then under vacuum from degassed activated molecular sieves, and finally under vacuum into the storage flask under a metal tap.

Pyridine (Eastman, spectroscopic grade) was distilled under vacuum onto and then from degassed activated molecular sieves, into a storage vessel under a metal tap. It was distilled into a graduated receiver and then into the polymerization vessel as required.

Sebacoyl and adipoyl chlorides (Eastman) and ethylene glycol (Fisher, reagent grade) were distilled onto and then from degassed activated molecular sieves. They were kept under vacuum until required, then transferred by syringe to

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(2) P. W. T. Willmott and F. W. Billmeyer, Jr., *Off. Dig. Federation Soc. Paint Technol.*, **35**, 847 (1963).

(3) E. A. Zavaglia, W. A. Mosher, and F. W. Billmeyer, Jr., *ibid.*, **37**, 229 (1965).

(4) E. A. Zavaglia and F. W. Billmeyer, Jr., *ibid.*, **36**, 221 (1964).

(5) P. S. Chang, E. A. Zavaglia, and F. W. Billmeyer, Jr., *ibid.*, **37**, 235 (1965).

(6) For general reviews of the synthesis of polyesters, see W. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry," Interscience Publishers, New York, N. Y., 1961; P. W. Morgan, "Condensation Polymers," John Wiley & Sons, Inc., New York, N. Y., 1965; or R. W. Lenz, "Organic Chemistry of Synthetic High Polymers," John Wiley & Sons, Inc., New York, N. Y., 1967.

(7) H. Mark and G. S. Whitby, Ed., "Collected Papers of Wallace Hume Carothers," Interscience Publishers, New York, N. Y., 1940.

(8) F. W. Billmeyer, Jr., and I. Katz, *Macromolecules*, **2**, 105 (1969).

(9) P. J. Flory and F. S. Leutner, U. S. Patent 2,589,687 and 2,589,688 (1952).

(10) E. R. Walsgrove and F. Reeder, British Patent 636,429 (1950).

(11) J. T. Dickson, H. P. W. Huggill, and J. C. Welch, British Patent 590,451 (1947).

a graduated tube on the polymerization apparatus and distilled into the main flask.

The molecular sieves (Linde 4A) were prepared by placing them in a distillation flask on the vacuum line and pumping down as far as possible with a diffusion pump. The flask was then heated with a yellow flame from a gas burner for several minutes while pumping was continued. The process was repeated once or twice until no further gas was evolved. After isolation from the vacuum line, the sieves were stored under vacuum until needed. Reagents to be purified were distilled onto the sieves, with the vacuum preserved at all times.

Syntheses

Direct Esterification. As described previously,[3] these reactions were carried out in a 500-ml glass reaction kettle equipped with nitrogen or vacuum connection, thermometer, stirrer and distillation head. The time–temperature cycle for the condensations was typically 6 hr at 175° with nitrogen atmosphere, 6–12 hr at 190–195° with nitrogen, and 6–10 hr at 165° with vacuum. Various catalysts such as litharge,[12] dibutyltin dilaurate, and tetraisopropyl titanate[13] (Du Pont) were used, the latter being the most efficient.

The major problems encountered in this method are, first, side reactions during the high-temperature step, and second, difficulty in removing the catalyst from the polymer. Polymer obtained with this synthesis tended to be brownish in bulk or on melting, but often looked deceptively white after precipitation. Since difunctional acids are used, side reactions leading to anhydride linkages in the polymer or to cyclic anhydrides can take place.

Acid Chloride Synthesis. This reaction was carried out at room temperature in chloroform solution, using pyridine as an acid acceptor to shift the equilibrium to high molecular weights. A 500-ml flask with Teflon-covered magnetic stirring bar was fitted with a "T" head, a 12-ml graduated tube and the vacuum line being attached to the other arms of the "T" by means of Teflon needle valves. The reagents (0.05 mol of acid chloride and glycol, 0.055 mol of pyridine, and 100 ml of chloroform) were distilled in, and the flask was sealed and stirred overnight. The isolated polymer was not as high in molecular weight as that obtained in the other syntheses, being capped by residual ethanol in the chloroform.

Aside from the difficulty of preparing dry alcohol-free chloroform, this scheme suffers from the need for extensive purification of the polymer to remove the pyridinium chloride. This was done by precipitating the polymer from chloroform solution with cold methanol, redissolving, and repeating several times.

Acid Exchange. The acid elimination reaction was attempted using ethylene diacetate and sebacic acid, with sodium carbonate being used as an acid acceptor. A stoichiometric mixture was heated until a solution formed, and Na_2CO_3 was gradually added. CO_2 was evolved over a period of time indicating progress of the reaction, but it proceeded slowly even at 160°. After 5 hr the mixture was a soft solid which on cooling hardened to a waxy solid which was slowly soluble in water. This indicated the presence of either a very low molecular weight polymer or large amounts of unreacted sebacic acid.

The reaction was repeated using TiO_2 as a catalyst. The results were similar. Large excesses of diacetate and Na_2CO_3 were also employed with no better results. It was concluded that purer materials and a better catalyst were required.

Ester Exchange. The ester exchange synthesis offers the possibility of much higher conversion due to the greater ease of removing the alcohol which results from the exchange. At a given temperature, under equilibrium conditions, removal of methanol could be expected to be at least an order of magnitude faster than removal of water. For various reasons, greater success was achieved with this reaction than with the others described, and it represents our preferred method for synthesizing the linear aliphatic polyesters.

The reaction was carried out in a 19-mm Pyrex tube equipped with a standard tapered joint and a side arm leading to the vacuum system. A nitrogen inlet tube ending in a capillary was provided to fit the joint at the top of the tube. The capillary ended near the bottom of the tube, and its size was adjusted to admit a slow continuous stream of bubbles even under vacuum.

In a typical synthesis, 0.2 g of hydroquinone was placed in the reaction tube to act as an antioxidant and 0.1 g of PbO (Fisher, reagent) was added as catalyst. Dimethyl sebacate and heptane-1,7-diol (0.05 mol of each) were then added. Pressure was slowly reduced with a nitrogen bleed. After the oxygen was swept out, the pressure was increased by slowly opening a tap on the vacuum line. With continued nitrogen bleed, the tube was placed in an oil bath, heated to 170°, and maintained there for 4 hr. The pressure in the line was slowly reduced until full vacuum was reached. The temperature was then slowly increased to 225° and maintained there overnight. The viscosity of the melt increased noticeably during the reaction, and at the end, a transparent viscous syrup was obtained, colored only by suspended PbO. On cooling (nitrogen bleed and under vacuum), a hard, white waxy solid resulted which melted at 80°. It was slowly soluble in chloroform, forming a clear viscous solution, which became yellow-brown on standing for 1 week. This may have been due to the oxidation of residual hydroquinone or oxidation of the polymer.

The synthesis was repeated using 0.05 mol each of dimethyl azealate and octane-1,8-diol. Again, a viscous syrup was produced which was slowly soluble in chloroform to form a clear solution. This solution also discolored on standing several days. Neither polymer sample was soluble in water.

It is not anticipated that most impurities present in the reactants should have a large effect on the final product other than changing the intended stoichiometry. Since the reaction is reversible and catalyst controlled, chain capping impurities may be distilled away. In using this synthesis, it is suggested that 10% excess of the more volatile component be used. Thus, if ethylene glycol were used, the proportions should be 0.055 mol of glycol and 0.050 mol of diester, respectively. In order to obtain maximum molecular weight ($\sim 10^5$), one

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(12) R. E. Wilfong, *J. Polym. Sci.*, **54**, 385 (1961).

(13) J. H. Haslam, U. S. Patent 2,822,348 (1958).

should compensate for the titer of the reactants, since the diesters are probably only 95–98% pure. Care should be taken to precipitate polymer to remove impurities such as hydroquinone. Solutions should be filtered before precipitation to remove PbO. Polymer should be dried overnight on the vacuum line with a cold trap.

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Gel Permeation Chromatography of Nominally Linear Aliphatic Polyesters

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In the course of studies[1–4] on structure–property relations in essentially linear aliphatic polyesters, we have examined the molecular weight distribution of some of these condensation polymers by gel permeation chromatography (gpc). Flory[5] has shown that, when made under equilibrium conditions and of sufficiently high molecular weight, these polymers should have the so-called "most probable" distribution of molecular weights, an important characteristic of which is that the breadth parameter $\bar{M}_w/\bar{M}_n = 2.0$. In our previous work,[3] we assumed this to be true for polyesters we synthesized by the direct esterification technique of Carothers.[6] The purpose of this paper is to point out that, probably as a result of side reactions during synthesis,[7] values of $\bar{M}_w/\bar{M}_n$ significantly higher than 2.0 are sometimes obtained in aliphatic polyesters made with nominally bifunctional reagents.

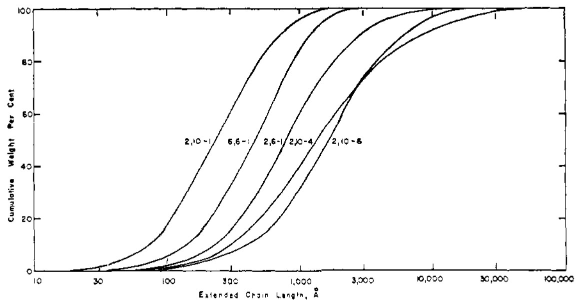

Figure 1. Cumulative molecular size distributions of nominally linear aliphatic polyesters by gel permeation chromatography.

Experimental Section

The synthesis of the polyesters of the 2,6; 2,8; 2,10; 4,6; and 6,6 types[8] used in this work has been described elsewhere.[3]

Gel permeation chromatography[9,10] was performed in a Waters Model 100 gel permeation chromatograph[11] using tetrahydrofuran as solvent at 37°. Columns with Waters designations 10^6, 10^5, 3×10^4, and 9×10^2 Å were used at a standard flow rate of 1 cc/min. Although tetrahydrofuran is not a good solvent for these polyesters, all of the samples were completely soluble at the operating temperature.

The column system had a plate count of 720 plates/foot. The system was calibrated with narrow-distribution polystyrenes,[12] and the convention of expressing results in terms of equivalent fully extended chain lengths was adopted. No corrections for axial dispersion (zone broadening) were made; it is not expected to have a major effect on the results with the relatively broad distribution samples studied. Cumulative and differential molecular weight distributions and weight- and number-average chain lengths were calculated on a digital computer, using the scheme described in the Waters instruction manual and by Cazes.[10]

For some of the samples, number-average molecular weights were determined by vapor phase osmometry[13] using a "Mechrolab" Model 302 vapor pressure osmometer.[14] Chloroform was used as solvent at 37°, and calibration was made with benzil.

Intrinsic viscosities were measured for a few of the polyesters in chloroform solution at 25°, using a Cannon–Ubbelohde viscometer, size 25.

Results

Table I summarizes the experimental results, expressed as number-average and weight-average chain lengths, $\bar{A}_n$ and $\bar{A}_w$, respectively. Values of $\bar{M}_n$, by vapor phase osmometry, and of the intrinsic viscosity are reported in Table II. A few typical cumulative molecular weight distributions are shown in Figure 1.

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(1) P. W. T. Willmott and F. W. Billmeyer, Jr., *Off. Dig. Federation Soc. Paint Technol.*, **35**, 847 (1963).

(2) E. A. Zavaglia, W. A. Mosher, and F. W. Billmeyer, Jr., *ibid.*, **37**, 229 (1965).

(3) E. A. Zavaglia and F. W. Billmeyer, Jr., *ibid.*, **36**, 221 (1964).

(4) P. S. Chang, E. A. Zavaglia, and F. W. Billmeyer, Jr., *ibid.*, **37**, 235 (1965).

(5) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(6) H. Mark and G. S. Whitby, Eds., "Collected Papers of Wallace Hume Carothers," Interscience Publishers, New York, N. Y., 1940.

(7) F. W. Billmeyer, Jr., and A. D. Eckard, *Macromolecules*, **2**, 103 (1969).

(8) See, for example, F. W. Billmeyer, Jr., "Textbook of Polymer Science," John Wiley & Sons, Inc., New York, N. Y., 1962, p 429.

(9) J. C. Moore, *J. Polym. Sci., Part A*, **2**, 835 (1964).

(10) J. Cazes, *J. Chem. Educ.*, **43**, A567, A625 (1966).

(11) L. E. Maley, *J. Polym. Sci., Part C*, **8**, 253 (1965).

(12) Pressure Chemicals Co., Pittsburgh, Pa., ArRo Laboratories, Joliet, Ill., or Waters Associates, Framingham, Mass.

(13) J. Van Dam, *Rec. Trav. Chim. Pays-Bas*, **83**, 129 (1964).

(14) F & M Scientific Division, Hewlett-Packard Corp., Avondale, Pa.