Review

Chemical Structure and Crystal Size in Polymer Single Crystals

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ABSTRACT: A review of research on polymer single crystals indicates that where other methods can be used to characterize the structural regularity of polymers, as in the case of polyethylene, there is a good correlation between structural regularity and the appearance of single crystals formed from dilute solutions of the polymers. Relatively large single crystals (maximum dimension greater than 5 μm) with smooth edges, sharp corners, and little random overgrowth are formed from polymers known to have very regular structures. This criterion has been used to classify the polymers that have been used for single crystal studies. All the known examples of relatively large, sharp crystals have been made with polymers that either have no points of asymmetry along the polymer chain (eight examples) or have been made in such a way as to have uniform stereoregularity at the points of asymmetry (*i.e.*, by isotactic polymerization) (six examples). Results are summarized for 17 polymers known to form irregular, small, or heavily overgrown objects under the conditions used for single crystal formation. In most cases it is possible to suggest the nature of the structural irregularity that prevents the formation of good crystals. Single crystal studies provide a good criterion for judging the regularity of the chemical structure of polymers.

Single crystals of organic polymers were first observed by Staudinger[1] in work on formaldehyde polymerization, and subsequently by Schlesinger and Leeper,[2] who worked with gutta percha. It was not until linear polyethylene became generally available that polymer single crystals came to be recognized as a form of matter that could be made in any laboratory and indeed was worthy of intensive scientific study.[3–5]

Results with Polyethylene. Free-radical polyethylene (known to have branched chains) and ethylene–α-olefin copolymers do not form the large, well-formed crystals that are characteristic of linear polyethylene.[3,6] It is important to distinguish between polymers that are *polyallomers*[7] (*i.e.*, with a chain made up of two or more different repeat units) and polymers that are *polyhomomers*[8] (*i.e.*, with all repeat units identical). The allomers may be *branching allomers*, *postpolymerization allomers*, or *copolymerization allomers*.

The effect of branching allomers on single crystal formation was first investigated by Till.[3] High-pressure polyethylene made by radical polymerization and having 21 methyl groups per 1000 carbon atoms did not form any single crystals under conditions of solution and cooling that produced single crystals with maximum dimension of 5 μm from linear polyethylene. Eppe, Fischer, and Stuart[6] subsequently compared electron photomicrographs of linear with high pressure (*i.e.*, branched) polyethylene. The latter formed small, flat objects, irregular in outline, with maximum dimension 3 μm. Samoilov, *et al.*,[9] also using branched polyethylene, obtained objects that were even smaller and more irregular.

The formation of diamond-shaped crystals can be a criterion for absence of branching. Machi and Toyota[10] used γ-radiation to make polyethylene with 2–10 methyl groups per 1000 carbon atoms. A fraction with 19,000 molecular weight formed diamond-shaped crystals, but the "crystals" from either the 64,000 or the 260,000 molecular weight fractions were oval. The authors conclude that "this difference may be caused by the difference in the degree of branching and other disruptions in the chain." Kilian and Fischer[11] studied the effect of chlorination after polymerization on the formation of polyethylene single crystals. With very light chlorination crystals formed with ragged edges and lumpy overgrowths. No crystals could be observed with products containing a C_2H_4:Cl ratio of 20:1. Job[12] graft-polymerized acrylonitrile onto high-density polyethylene and then fractionated to remove material low in nitrogen. Crystallization became progressively more difficult as the proportion of nitrogen (*i.e.*, the proportion of allomer) increased. After the first few fractions, only rudimentary structures were obtained.

Holdsworth and Keller[13] have made the most extensive study of the effect of allomers introduced by co-

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(1) H. Staudinger, H. Johner, R. Signer, G. Mie, and J. Hengstenberg, *Z. Physik. Chem.*, **26**, 425 (1927).

(2) W. Schlesinger and H. M. Leeper, *J. Polym. Sci.*, **11**, 203 (1953).

(3) P. H. Till, *ibid.*, **24**, 301 (1957).

(4) A. Keller, *Phil. Mag.*, **2**, 1171 (1957).

(5) E. W. Fischer, *Z. Naturforsch.*, **12a**, 753 (1957).

(6) R. Eppe, E. W. Fischer, and H. A. Stuart, *J. Polym. Sci.*, **34**, 721 (1959).

(7) H. J. Hagemeyer and M. B. Edwards, *ibid.*, *Part C*, **4**, 731 (1964).

(8) H. K. Livingston and J. E. Nyenhuis, *J. Chem. Doc.*, **5**, 89 (1965).

(9) S. M. Samoilov, M. B. Konstantinopolskaya, Z. Ya. Berestneva, and V. A. Kargin, *Polym. Sci. USSR*, **9**, 1473 (1968).

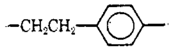
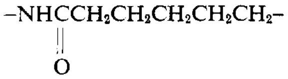
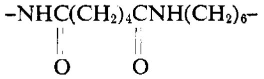
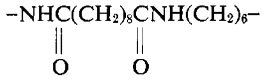
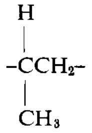
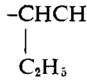
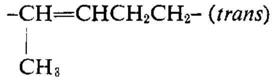
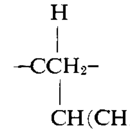
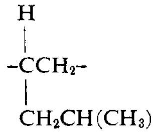
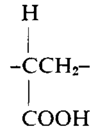
(10) S. Machi and N. Toyota, *J. Polym. Sci., Part A-2*, **6**, 289 (1968).

(11) H. G. Kilian and E. W. Fischer, *Kolloid-Z. Z. Polym.*, **11**, 40 (1966).

(12) C. Job, *J. Polym. Sci., Part C*, **16**, 2393 (1967).

(13) P. J. Holdsworth and A. Keller, *ibid.*, *Part B*, **5**, 605 (1967)

TABLE I
POLYMERS FORMING SINGLE CRYSTALS OF REGULAR SHAPE

Repeating unit in polymer	Max dimension of crystals	Crystal shape	Description of polymer sample from which crystals were prepared	Ref
A. All groups R equivalent				
$-CH_2-$	5 μm	Sharp diamond shape	Ziegler process; typically 1.5 methyl groups per 1000 C atoms	3–6, 13
	8–10 μm	Rectangles or hexagons, depending on crystal habit; hexagons have very sharp edges	Linear polymer made by mild pyrolysis of di-*p*-xylylene	*a*
$-OCH_2-$	10 μm[q]	Hexagons and stars, frequently with perfect spiral overgrowths; all edges very sharp	Commercial polymer ("Delrin" acetal resin)	*b, c*
$-OCH_2CH_2-$	5 μm	Sharp rectangles with step overgrowths	Any of several commercial products; molecular weights average 10,000 for some samples; 1,000,000 for others	*d*
$-OCH_2C(CH_2Cl)_2CH_2-$	6 μm	Sharp diamond-shaped crystals with few very regular overgrowths	Commercial polymer ["Penton" bis(chloromethyl)oxetane polymer]	*e*
 $-NH\underset{\underset{O}{\Vert}}{C}CH_2CH_2CH_2CH_2CH_2-$	12 μm	Sharp diamond-shaped crystals	Preparative information not given	*f*
 $-NH\underset{\underset{O}{\Vert}}{C}(CH_2)_4\underset{\underset{O}{\Vert}}{C}NH(CH_2)_6-$	10 μm	Ribbonlike lamella	Preparative information not given	*g*
 $-NH\underset{\underset{O}{\Vert}}{C}(CH_2)_8\underset{\underset{O}{\Vert}}{C}NH(CH_2)_6-$	8 μm	Straight rods	Polymerized by interfacial polycondensation	*h*
B. R-Nonequivalent groups present; all such groups in the same stereochemical orientation				
 $-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2-$	5 μm	Elongated platelets, roughly rectangular, with oriented globular overgrowths	Best results with experimental isotactic polypropylene that had subsequently been fractionated	*i, j*
 $-\underset{\underset{C_2H_5}{|}}{C}HCH_2-$	10 μm	Squares with fairly regular outline	Specially prepared isotactic poly-1-butene	*k*
 $-\underset{\underset{CH_3}{|}}{C}H{=}CHCH_2CH_2-$ (*trans*)	0.35 mm[q]	Sharp-edged polyhedra	Natural product; gutta percha Pahang	2
 $-\overset{\overset{H}{|}}{\underset{\underset{CH(CH_3)_2}{|}}{C}}CH_2-$	16 μm	Rectangles with fairly sharp edges and a few overgrowths	Made from 3-methyl-1-butene; process not described but must have used Ziegler catalysts	*l*
 $-\overset{\overset{H}{|}}{\underset{\underset{CH_2CH(CH_3)_2}{|}}{C}}CH_2-$	13 μm	Rectangles of regular outline; some crystals are exceptionally sharp in outline	Earliest work was with a laboratory preparation whose physical properties compared favorably with Natta's original isotactic polymer; subsequently work with Tennessee Eastman's commercial poly(4-methyl-1-pentene) gave even better crystals	*m, n*
 $-\overset{\overset{H}{|}}{\underset{\underset{COOH}{|}}{C}}CH_2-$	8 μm	Diamond-shaped crystals with sharp edges	Polymer made by hydrolysis of isotactic polyacrylates (either isopropyl or *t*-butyl ester)	*o, p*

[a] W. D. Niegisch, *J. Appl. Phys.*, **37**, 4041 (1966). [b] P. H. Geil, N. K. J. Symons, and R. G. Scott, *ibid.*, **30**, 1516 (1959). [c] D. H. Reneker and P. H. Geil, *ibid.*, **31**, 1916 (1960). [d] F. J. Balta-Calleja and A. Keller, *J. Polym. Sci., Part A*, **2**, 2171 (1964). [e] P. H. Geil, *Polymer*, **4**, 404 (1963). [f] P. H. Geil, *J. Polym. Sci., Part A*, **2**, 3857 (1964). [g] P. H. Geil, "Polymer Single Crystals," Interscience Publishers, New York, N. Y., 1963, pp 169, 183. [h] H. K. Livingston, *J. Polym. Sci., Part C*, **18**, 105 (1967). [i] B. G. Ranby, F. F. Morehead, and N. M. Walter, *ibid.*, **44**, 349 (1960). [j] D. R. Morrow, J. A. Sauer, and A. E. Woodward, *ibid., Part B*, **3**, 463 (1965). [k] V. F. Holland and R. L. Miller, *J. Appl. Phys.*, **35**, 3241 (1964). [l] H. Utsonimiya, N. Kawasaki, M. Niinomi, and M. Takayanagi, *J. Polym. Sci., Part B*, **5**, 907 (1967). [m] F. C. Frank, A. Keller, and A. O'Connor, *Phil. Mag.*, **4**, 200 (1959). [n] D. C. Bassett, *ibid.*, **10**, 595 (1964). [o] V. A. Kargin, V. A. Kabanov, S. Ya. Mirlina, and A. V. Vlasov, *Polym. Sci. USSR*, **3**, 28 (1962). [p] M. L. Miller, M. C. Botty, and C. E. Rauhut, *J. Colloid Sci.*, **15**, 83 (1960). [q] Studied by light microscopy; in all other cases electron microscopes were used.

TABLE II
POLYMERS FORMING SMALL OR IRREGULAR "SINGLE CRYSTALS"

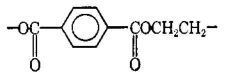
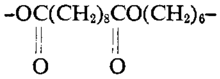
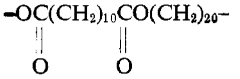
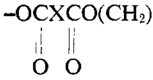
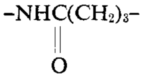
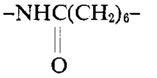
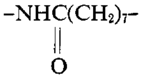
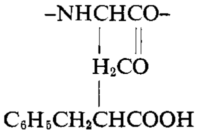
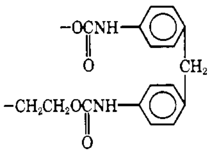
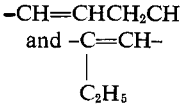
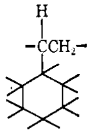
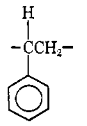
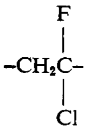
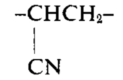
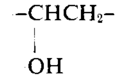
Repeating unit in the polymer	Max dimension of crystals	Crystal shape	Description of polymer sample from which crystals were prepared	Ref
A. All groups R equivalent				
$-CF_2-$	3 μm	Spiral growth, hexagons with ragged edges	No preparative details given	*a*
$-CF_2CH_2-$	2 μm	Almost round and corrugated	Commercial poly(vinylidene fluoride)	*b*, *c*
	4 μm	Edges not sharp, heavy overgrowths	Commercial 2T polyester	*d*
 $-O\underset{\underset{O}{\|}}{C}(CH_2)_8\underset{\underset{O}{\|}}{C}O(CH_2)_6-$	2 μm	Irregular edges, generally hexagonal outline; step growths	Poly(hexamethylene sebacate); no preparative details given	*e*
 $-O\underset{\underset{O}{\|}}{C}(CH_2)_{10}\underset{\underset{O}{\|}}{C}O(CH_2)_{20}-$	3 μm	Stacks of diamond-shaped crystals with slightly wavy edges	Poly(eicosamethylene dodecanedicarboxylate); no preparative details given	*e*
 $-O\underset{\underset{O}{\|}}{C}X\underset{\underset{O}{\|}}{C}O(CH_2)_{10}-$	3 μm	Polygons with extensive step growth	Several different polyesters of 1,10-decanediol were made but the electron photomicrographs are not specifically identified as to the polymer used	*f*
 $-NH\underset{\underset{O}{\|}}{C}(CH_2)_3-$	1 μm	Almost round and corrugated; see text	Nylon 4, made by anionic polymerization of pyrrolidone	*g*
 $-NH\underset{\underset{O}{\|}}{C}(CH_2)_6-$	2 μm	Roughly rectangular; heavy overgrowth	None given	*a*
 $-NH\underset{\underset{O}{\|}}{C}(CH_2)_7-$	3 μm	Diamond-shaped crystals with striated surface; step growth	None given	*a*
	3 μm	Twisted rods	Prepared by the Technical Institute of Asahikasei, presumably by conventional polypeptide synthesis; both D and L forms were present and twists of the two different "handednesses" were observed	*h*
	5 μm	Irregular leaves, heavily overgrown	No preparative information given, but the starting materials were ethylene glycol and bis(*p*-isocyanatophenyl)methane	*i*
B. R-Nonequivalent groups present				
 $-CH{=}CHCH_2CH_2-$ and $-\underset{\underset{C_2H_5}{\vert}}{C}{=}CH-$	6 μm	Ovals with rough edges and heavy overgrowths	99% *trans*-1,4-polybutadiene and 1% 1,2-polybutadiene	*j*
	9 μm	Irregular edges on roughly rectangular shapes with heavy overgrowths	Polymer made from vinylcyclohexane; process not described	*k*
	3 μm	Irregular objects with diamond-like outline	Isotactic polystyrene	*l*, *m*
 $-CH_2\overset{\overset{F}{\vert}}{\underset{\underset{Cl}{\vert}}{C}}-$	1 μm	Some rectangles, some irregular shapes	No preparative information given	*n*

TABLE II (*Continued*)

Repeating unit in the polymer	Max dimension of crystals	Crystal shape	Description of polymer sample from which crystals were prepared	Ref
 $-CH(CN)CH_2-$	3 μm	See text	See text	*o–q*
 $-CH(OH)CH_2-$	5 μm	Narrow strips with two curving faces	Poly(vinyl acetate) was saponified to form the poly(vinyl alcohol); commercial nonstereospecific poly(vinyl acetate) was used	*r, s*

[a] See Table I, footnote *g*. [b] K. Sakaoku and A. Peterlin, *J. Macromol. Sci., Part B*, **1**, 401 (1967). [c] K. Okuda, T. Yoshida, M. Sugita, and M. Asahina, *J. Polym. Sci., Part B*, **5**, 465 (1967). [d] N. Hirai, S. Fujita, K. Yamamoto, and Y. Yamashita, *Intern. Chem. Eng.*, **4**, 535 (1964). [e] K. Z. Gumargalieva and E. M. Belavtseva, *Polym. Sci. USSR*, **8**, 1769 (1967). [f] Yu. V. Mnyukh, E. M. Belavtseva, and A. I. Kitaigorodskii, *Dokl. Akad. Nauk SSSR*, **133**, 1132 (1960). [g] K. Sakaoku, H. G. Clark, and A. Peterlin, *J. Polym. Sci., Part A-2*, **6**, 1035 (1968). [h] N. Hirai, *Kobunshi Kagaku*, **21**, 193 (1964). [i] B. V. Vasilev, O. G. Tarakanov, A. I. Demina, and A. I. Shirobokova, *Polym. Sci. USSR*, **8**, 1031 (1967). [j] M. Takayanagi, K. Imada, A. Nagai, T. Tatsumi, and T. Matsuo, *J. Polym. Sci., Part C*, **16**, 867 (1967). [k] J. D. Hutchinson, *J. Polym. Sci., Part A*, **3**, 2710 (1965). [l] V. A. Kargin, N. F. Bakeev, L.-S. Li, and T. S. Ochapovskaya, *Vysokomol. Soedin.*, **2**, 1280 (1960). [m] V. A. Kargin, T. A. Koretskaya, and T. A. Bogaevskaya, *Polym. Sci. USSR*, **6**, 489 (1965). [n] V. A. Kargin, N. F. Bakeev, and L.-S. Li, *Vysokomol. Soedin.*, **3**, 1100 (1961). [o] V. F. Holland, S. B. Mitchell, W. L. Hunter, and P. H. Lindenmeyer, *J. Polym. Sci.*, **62**, 145 (1962). [p] R. Chiang, J. H. Rhodes, and V. F. Holland, *ibid., Part A*, **3**, 479 (1965). [q] P. H. Lindenmeyer and R. Hosemann, *J. Appl. Phys.*, **34**, 42 (1963). [r] J. F. Kenney and V. F. Holland, *J. Polym. Sci., Part A-1*, **4**, 699 (1966). [s] K. Tsuboi and T. Mochizuki, *Kobunshi Kagaku*, **23**, 636 (1966).

polymerization of propylene or 1-butene with ethylene. With 30 alkyl groups per 1000 carbon atoms, the electron microscope shows only small objects, possibly spherulitelike but not well defined, with no dimension greater than 1 μm. When linear polyethylene was mixed with a high-propylene copolymer and single crystal formation attempted, the polyhomomer crystallized first and the polyallomer then crystallized on the oriented border of the large, regular polyethylene crystals. Except under special circumstances, one expects to find a direct relation between chemical purity and crystal size and perfection. Balta, *et al.*,[14] have measured the magnetic susceptibility of the material collected when polyethylene was precipitated from very dilute xylene solutions by cooling. For samples varying from 1 to 30 in methyl groups per 1000 carbon atoms, the magnetic susceptibility was a linear function of the methyl group content, approaching the value for polyethylene melts with increasing branching. Disorder increased with branching, and disorder obviously limits crystal size.

Crystallization can be used to isolate polyhomomers from mixtures. As mentioned above, Holdsworth and Keller[13] separated polyhomomer first from the polymer mixture that they prepared. Pennings[15] isolated pure polyethylene from an ethylene–propylene block copolymer by cooling a tetrachloroethylene solution of the copolymer below the melting point of polyethylene but above the melting point of polypropylene.

Factors Influencing the Regularity of Chemical Structure. The formation of single crystals has been studied with polymers other than polyethylene. Garber and Geil[16] have done this for polyallomers containing a major proportion of $-OCH_2-$ mers and a minor proportion of $-OCH_2CH_2-$ mers. As the amount of the latter increased, the growth faces on the single crystals became less regular and the number of overgrowths increased dramatically. This work dealt with experiments in which the allomer was introduced deliberately. Whenever an addition homopolymerization or a "two-component" polycondensaton is run, one should consider the several ways in which such reactions may fail to give the expected polyhomomer. Chain transfer is important in the mechanism of radical-initiated polymerization and frequently leads to branching. The occurrence of chain branching in free-radical polymerization, first postulated by Flory,[17] is now completely accepted as an important contributor to the mechanism of polymerization. Bryant[18] has concluded that there is no reliable evidence for side chains in $(-CF_2-)_n$ polymer, probably because kinetics do not favor the breaking of C–F bonds. However, in polymers containing C–H bonds, chain branching is expected whenever radical initiation is used. Atkins and Billmeyer[19] have summarized the evidence for chain transfer in cationic polymerization of styrene. Chain transfer does cause chain branching in polystyrene, especially at high yields. It is a possibility in other cationic polymerizations, but is not generally associated with anionic radical polymerization. The reports of single crystal formation from polymers

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(14) F. J. Balta-Calleja, H. Cackovic, R. Hosemann, and W. Wilke, *Kolloid-Z. Z. Polym.*, **6**, 118 (1965).
(15) A. J. Pennings, *J. Polym. Sci., Part C*, **16**, 1799 (1967).
(16) C. A. Garber and P. H. Geil, *Makromol. Chem.*, **113**, 236 (1968).
(17) P. J. Flory, *J. Amer. Chem. Soc.*, **59**, 241 (1937).
(18) W. M. D. Bryant, *J. Polym. Sci.*, **56**, 277 (1962).
(19) J. T. Atkins and F. W. Billmeyer, *J. Phys. Chem.*, **63**, 1966 (1959).

made with Ziegler–Natta catalysts (*cf.* Natta[20]) indicate that chain branching is not to be expected with this mechanism.

Allomers can also result from *stereoisomerism.* In a carbon chain, the various $-CR_1R_2-$ groups along the chain can be either R equivalent ($R_1 = R_2$) or R nonequivalent ($R_1 \neq R_2$). An alternate definition states that the chain atom with its substituent groups does contain an improper axis of symmetry (R equivalent) or does not (R nonequivalent). A polymer in which the repeat units contain R-nonequivalent $-CR_1R_2-$ groups can be a polyallomer because it contains *stereochemical allomers.* However, if all R-nonequivalent groups have the same orientation of R_1 and R_2 with respect to the chain, there are no stereochemical allomers and the polymer is a polyhomomer (in the simplest case, it will be an isotactic polymer). If a $-CH_2CR_1R_2-$ repeat unit has the R-nonequivalent groups arranged with perfect alternation, then the polymer is a polyhomomer in which the repeat unit contains four carbon chain atoms (and it is a syndiotactic polymer).

We can conclude that *branching allomers* are to be expected in polymers made by most radical addition polymerizations and some cationic addition polymerizations, but not in polymers made by anionic or Ziegler–Natta addition polymerization or by condensation polymerization. *Postpolymerization allomers* can be avoided by eliminating all possible causes of chemical reaction (*i.e.*, actinic light) that the polymer might otherwise encounter. *Copolymerization allomers* may result from impurities in the monomers and can only be minimized by working with polymerization systems in which all the components that are used are of excellent purity. *Stereochemical allomers* will not occur if the polymer contains no R-nonequivalent groups or has all its R-nonequivalent groups in a regular arrangement.

Summary of Published Data on Polymer Single Crystals. Many studies of polymer single crystals have been published since the 1957 discovery that Ziegler polyethylene formed crystals of regular habit. It might be supposed that a tremendous variety of polymers had been successfully induced to form single crystals. Such is not the case, at least if one is to judge by the results that have been published. Table I lists the 14 polymers for which single crystals of regular shape and maximum dimension of 5 μm or more have been prepared. It is significant that eight of these contain only R-equivalent groups. Of the other six, one is a natural product and the others were all made by Ziegler–Natta polymerization. Most work with polypropylene made by the Natta process has produced only small, irregular crystals. Morrow, *et al.*,[21] obtained crystals as large as 5 μm by starting with fractionated polymer from laboratory-polymerized propylene. With commercial isotactic polypropylene, they were only able to obtain a few small platelets with heavy overgrowth.

Experiments designed to produce single crystals but yielding small or irregular objects are summarized in Table II. The irregularity of the objects observed on crystallizing commercial poly(tetrafluoroethylene) from solutions is unexpected. In an extensive study Symons[22] was able to obtain only star-shaped objects that were not well ordered or dendrites. Two possible explanations may be offered. The polymer may in fact be branched, even though kinetic considerations have been offered[18] as proof that it cannot be. Alternatively, the phase transitions that occur near room temperature[23] may have interfered with single crystal formation, in which case a change in crystallization procedure may give large crystals.

Holland, *et al.*,[24] published electron photomicrographs of polyacrylonitrile objects with irregular outline and rough surface, 3 μm in maximum dimension, formed from radical-initiated polymer. Polyacrylonitrile prepared by coordination polymerization gave similar electron photomicrographs, in the work of Chiang, *et al.*[25] Lindenmeyer and Hosemann[26] interpreted these and other results as showing that polyacrylonitrile was "highly disordered" and not truly crystalline.

Single crystal formation has proved to be quite difficult for poly(vinyl chloride). Vishnevskaya, *et al.*,[27] on attempted crystallization of the coordination polymer, formed solids that gave amorphous electron diffraction patterns. The Burleigh method[28] for preparing poly(vinyl chloride) with average degree of polymerization 40 was used by Smith and Wilkes,[29] who made single crystals 2 μm in maximum dimension with rounded corners but very little overgrowth. The preparation of large single crystals from high molecular weight poly(vinyl chloride) has not yet been reported.

It is not intended to imply that copolymers never form regular single crystals. Lotz, *et al.*,[30] prepared single crystals from a block copolymer consisting of two blocks. One block was poly(oxyethylene), in which all groups are R equivalent. The other block was atactic polystyrene, in which there are many R-nonequivalent groups. The crystals consisted of poly(oxyethylene) single crystals sandwiched between amorphous polystyrene segments.

Another type of copolymer is the biological material (protein crystals or nucleic acid crystals) well known in the biochemical literature. Vainshtein[31] characterizes the crystalline biological polymers as "composite chain molecules, bundles of chains, and complex molecules." He considers it impossible for clews formed by random folding and coiling of molecules under the

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(20) G. Natta, *Makromol. Chem.*, **35**, 94 (1960).

(21) See Table I, footnote *j*.

(22) N. K. J. Symons, *J. Polym. Sci.*, **51**, S21 (1961).

(23) C. A. Sperati and H. W. Starkweather, *Fortschr. Hochpolym. Forsch.*, **2**, 465 (1961).

(24) See Table II, footnote *o*.

(25) See Table II, footnote *p*.

(26) See Table II, footnote *q*.

(27) I. N. Vishnevskaya, K. S. Minsker, and V. A. Kargin, *Polym. Sci. USSR*, **8**, 944 (1967).

(28) P. H. Burleigh, *J. Amer. Chem. Soc.*, **82**, 749 (1960).

(29) R. W. Smith and C. E. Wilkes, *J. Polym. Sci., Part B*, **5**, 433 (1967).

(30) B. Lotz, A. J. Kovacs, G. A. Bassett, and A. Keller, *Kolloid-Z. Z. Polym.*, **9**, 115 (1966).

(31) B. K. Vainshtein, "Diffraction of X-Rays by Chain Molecules," Elsevier Publishing Co., Amsterdam, 1966, pp 62–74.

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

$$n\mathrm{HOOC(CH_2)_xCOOH} + n\mathrm{HO(CH_2)_yOH} \longrightarrow \mathrm{H[OCO(CH_2)_xCOO(CH_2)_y]_nOH} + (n-1)\mathrm{H_2O}$$

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]

$$n\mathrm{ClOC(CH_2)_xCOCl} + n\mathrm{HO(CH_2)_yOH} \longrightarrow \mathrm{Cl[OC(CH_2)_xCOO(CH_2)_y]_nOH} + (n-1)\mathrm{HCl}$$

2. acid exchange[10]

$$n\mathrm{HOOC(CH_2)_xCOOH} + n\mathrm{CH_3COO(CH_2)_yOCOCH_3} \longrightarrow \mathrm{H[OCO(CH_2)_xCOO(CH_2)_y]_nOCOCH_3} + (n-1)\mathrm{CH_3COOH}$$

3. ester exchange[11]

$$n\mathrm{CH_3OCO(CH_2)_xCOOCH_3} + n\mathrm{HO(CH_2)_yOH} \longrightarrow \mathrm{CH_3[OCO(CH_2)_xCOO(CH_2)_y]_nOH} + (n-1)\mathrm{CH_3OH}$$

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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(1) The Donnan Laboratories, University of Liverpool, Liverpool, England.

(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).