

7 Crystallization and Material Properties of Polyhydroxyalkanoates

Prof. Dr. Robert H. Marchessault¹, Prof. Dr. Ga-er Yu²

¹ Pulp and Paper Research Center, Department of Chemistry, McGill University,
3420 University Street, Montreal, QC, Canada. Tel: +1 514 398-6276;
Fax: +1 514 398-7249; E-mail: ch21@musica.mcgill.ca

² Pulp and Paper Research Center, Department of Chemistry, McGill University,
3420 University Street, Montreal, QC, Canada. Tel: +1 514 398-6276;
Fax: +1 514 398-7249; E-mail: ch21@musica.mcgill.ca

1	Introduction	158
2	Historical Outline	160
3	General Use Properties	164
4	Optical Rotation of PHAs	167
5	Crystalline Unit Cell and Conformation of Bacterial Poly(3HB) and Poly(3HV)	169
6	Crystalline Structure of Syndiotactic Poly(3HB)	172
7	Crystalline Conformation of Poly(4-hydroxybutyrate)	173
8	Crystalline Structure and Properties of MCL-PHA	175
9	Folded Chain Lamellar Single Crystals	177
10	Splintering of Poly(3HB) Single Crystals by Depolymerases	180
11	Molecular Chirality and Polymer Morphology	181
12	Kinetics of Crystallization of PHA	184
13	Thermal Degradation	185

14	Crystalline Structure of Poly(3HB) Oligomers	187
15	Dependence of Lamellar Thickness and T_m on the Molecular Weight of Poly(3HB)	189
16	Chemical Degradation of Lamellar Poly(3HB) Crystals	192
17	Outlook and Perspectives	194
18	References	196

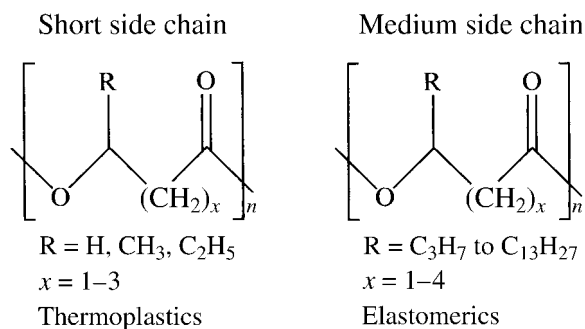
$[\alpha]^{25}$	specific optical rotation at a given temperature and wavelength
CD	circular dichroism
CP/MAS	cross-polarization magic angle spinning
d	interplanar distance in crystal structure
FTIR	Fourier transform infrared spectroscopy
MCL	medium chain length
M_n	number average molecular weight
M_w	weight average molecular weight
NMR	nuclear magnetic resonance
PET	poly(ethylene terephthalate)
PHA	polyhydroxyalkanoate
PHO	poly(3-hydroxyoctanoate)
Poly(3HB)	poly(3-hydroxybutyrate)
Poly(3HB-co-3HV)	poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
Poly(3HP)	poly(3-hydroxypropionate)
Poly(3HV)	poly(3-hydroxyvalerate)
Poly(4HB)	poly(4-hydroxybutyrate)
ORD	optical rotatory dispersion
R	reliability factor
R	absolute configuration of a carbon atom
syn	syndiotactic
T_g	glass transition temperature
T_m	melting temperature
TGA	thermogravimetric analysis

1 Introduction

Many bacterial species are able to accumulate a water-insoluble, dense, crystalline granule which biochemists originally referred to as “lipid poly(3-hydroxybutyrate)” (Poly(3HB)). More recently, it has become

known that this molecule is but one member of a broad family termed poly(3-hydroxyalkanoates) (PHAs), which have the general formula:

The field of PHAs covers: (1) microbiological production with its content of biochemistry and genetic engineering, (2) polymer chemistry of linear aliphatic polyesters



with implied chemical modification, synthesis and degradation, features, (3) industrial uses and relation to material properties. Surveys of the above topics can be found in reviews (Anderson and Dawes, 1990; Braunegg et al., 1998; Marchessault et al., 1988; Sudesh et al., 2000), monographs (Doi, 1990), conference proceedings of the biennial International Symposium on Biological Polyesters, and book chapters (Holmes, 1987; Hocking and Marchessault, 1994). This chapter collects solid-state characteristics and physical properties which are used to characterize PHA material. Some of these properties are used in the proof of structure of Poly(3HB), while others are critical in commercial developments based on PHA. Consequently, the range of topics covered is broad, but not comprehensive enough to satisfy all readers.

An aliphatic polyester such as Poly(3HB) would seem inevitably to have been synthesized by early workers in the field of synthetic polymers. Not so!, said the literature when it was dutifully, but not exhaustively examined in 1962, as polymer chemists started to take an interest (Alper et al., 1963). The obvious source to examine was *The Collected Papers of Wallace Hume Carothers* (Mark and Whitby, 1940), the genius behind corporate Dupont's Nylon 66 invention. However, his early studies on aliphatic

polyesters based on condensation of ω-hydroxyacids as well as diols and diacids, was a step-reaction process that does not convert the product into high molecular weights. For this reason Nylon 66, with its strong intermolecular hydrogen bonds, was chosen by Dupont to make the first man-made synthetic fiber. The intermolecular secondary forces allowed Nylon 66 to act as a high-molecular-weight material, as needed for fiber strength. One had to wait for the advances in polymer chemistry and the technical scaffold of biotechnology to appreciate the very high-molecular-weight polyester which was available as the natural plastic: poly(*R*-(-)-3-hydroxybutyric acid). Made as a carbon reserve by an enzymatic polymerization, a coordination chain reaction reminiscent of the Ziegler–Natta catalytic mechanism for polyolefins, Poly(3HB) was compared to isotactic polypropylene by polymer chemists. However, this non-petrochemical aliphatic polyester is truly part of the green chemistry revolution with numerous options for its fermentation biosynthesis as a homopolymer or random copolymers (Table 1). Thanks to faultless stereochemistry, Poly(3HB) and its homologue poly(*R*-(-)-3-hydroxyvalerate) (Poly(3HV)) are high crystallinity materials in all their fabricated forms. The crystalline structures of the more commonly occurring repeating units in

Tab. 1 PHA random copolymers produced by *A. eutrophus* from various carbon sources (Doi, 1990)

Carbon sources	Random copolymer
Propionic acid Pentanoic acid	 $(R)\text{-}3\text{HB}$ $(R)\text{-}3\text{HV}$
4-Hydroxybutyric acid γ -Butyrolactone 1,4-Butanediol 1,6-Hexanediol 1,8-Octanediol 1,10-Decanediol 1,12-Dodecanediol	 $(R)\text{-}3\text{HB}$ 4HB
3-Hydroxypropionic acid 1,5-Pentanediol 1,7-Heptanediol 1,9-Nonanediol	 $(R)\text{-}3\text{HB}$ 3HP

PHA homopolymers and copolymers shown in Table 1 have recently been reviewed by Iwata and Doi (1999).

With the invention of isotactic polypropylene, Nobelist G. Natta said that: "Nature has lost a monopoly". However, Nature did not go out of business and the environmental imperatives of this planet remind us that now is an ideal time to understand the properties of PHA, armed with the polymer science of the past half century. PHA occupies a unique place among biopolymers because of its biodegradability and thermo-plasticity.

2

Historical Outline

The discovery of Poly(3HB) dates back to the 1920s when Maurice Lemoigne (1923), a chemist and bacteriologist at the Lille branch of the Pasteur Institute, observed that this granular bacterial component was not ether

soluble, as is normal for lipids. Its identification as a polycondensation product of *R*-(-)-3-hydroxybutyric acid proceeded without any of the historical controversies which marked the early establishment of the polymer structure concept (Morris, 1986). Using microscopic observations, saponification numbers, and autolysis (to produce oligomers whose solubility and melting point (T_m) variation were correlated with molecular size), Lemoigne (1923, 1924, 1925, 1926, 1927) proposed a polyester structure with formula $(C_4H_6O_2)_n$. Furthermore, he recorded its optical rotation to establish the chiral properties of this natural material. Colleagues started publishing independently from the late 1940s onwards, e.g. Gavard (1966a,b, 1967), Kepes and Péaud-Lenoël (1952), and Hauttecoeur et al. (1972a,b, 1975), most frequently in *C. R. Rend. Acad. Sci.* As stated by Dawes (1986) in his monograph on Poly(3HB) "it is an ideal reserve material because it is a highly reduced intracellular molecule and being

virtually insoluble exerts negligible osmotic pressure". The majority of bacteria accumulate Poly(3HB) in response to physiological stress (e.g. nitrogen deficiency) and observations on Poly(3HB) in the bacteriological literature (Anderson and Dawes, 1990) suggest that it is a primary product of carbon assimilation, like starch and glycogen. Noteworthy is the fact that Poly(3HB) granules are found with a membrane containing both polymerase and depolymerase enzymes (Merrick and Doudoroff, 1961). This means that the granules can be considered as complete subsystems of the cell, able to respond synthetically or degradatively to physiological stresses.

The academic contact between microbiologist and polymer researchers started around 1961 at Syracuse University, when polymer chemists at the State University of New York, College of Forestry, and microbiologists at Syracuse University began exchanging ideas and experimental methodology. The first publication from this synergy (Alper et al., 1963) clearly places Poly(3HB) and isotactic polypropylene on the same polymeric platform. The common denomi-

nator was the isotacticity and helical crystalline conformation. The methodology of X-ray fiber diffraction, lamellar single crystal texture, and electron microscopy demonstrated that Poly(3HB) was a true thermoplastic. The chiral nature of the Poly(3HB) was supported by a *bona fide* optical rotatory dispersion curve (see below). The degradative effect of alkaline hypochlorite, used for isolating the polymer granules, was demonstrated by intrinsic viscosity and absolute molecular weight measurements. A second publication from the Syracuse synergy (Lundgren et al., 1965) was a broad survey of 17 Poly(3HB) samples submitted from 10 different research groups. Three of the samples from different species had relative molecular weights of 59,000, 128,000, and 25,6000 compared to 1000–22,000 for the others. All but one of the low-molecular-weight samples corresponded to hypochlorite treatment for isolation. Solvent extraction provided high molecular weights.

Collaborative contributions from Syracuse continued until 1970 covering enzymology (Lundgren et al., 1964) and Poly(3HB) nascent morphology (Ellar et al., 1968). A

Biography. Maurice Lemoigne (1883–1967)

Born	Paris, France 16 December 1883
Studies	
1903–1906	Institut National Agronomique: Ingénieur (Chemistry & Bacteriology)
1908	Institut Pasteur at Saigon
1913	PhD „ <i>Bacillus subtilis</i> in sewer water purification“ (Director: P. Mazé, élève de Emile Duclaux)
Career	
1914–1919	“Volontaire”
1924	Directeur: Laboratoire des Fermentations, Institut Pasteur <i>and</i> Station Agronomique du Nord (both at Lille, France)
1928–1939	Professeur of Analytical and Agricultural Chemistry Institut National Agronomique (Paris, France)
1939	“ Chef ” Fermentations et Chimie Agricole Institut Pasteur, Paris
1952	Electred to Academie des Sciences (numerous honours, e.g. “Chevalier and Commandeur Légion d’Honneur”)
Sources:	Notice Nécrologique, Ann. Inst. Nat. Agronomique 1967, 5 (Nouvelle Série); C. R. Acad. Sci. Paris 264, 12 June 1967; Autobiographical files Institute Pasteur.

similar synergy developed later at the University of Massachusetts (Amherst, MA) with a high level of innovative developments and training benefits deriving therefrom. In the UK, ICI orchestrated a strong industry–university collaboration from the 1980s once their commercialization strategy was launched (Holmes, 1987).

After the early studies at the Lille branch of the Pasteur Institute establishing the chemical and macromolecular structure of Poly(3HB) (Bréchet and Desvaux, 1967), an understanding of the biosynthesis and enzymatic degradation processes was established by North American researchers who literally rediscovered Poly(3HB) (Anderson and Dawes, 1990). The potential of this unusual material for commercial applications became apparent in the early 1960s as a major industrial concern (W. R. Grace and Co.) with a business commitment in film for packaging demonstrated (Baptist, 1962) the plastics potential of Poly(3HB), including production methods to yield a high-molec-

ular-weight product. Its similarity to the structure of polypropylene, which like Poly(3HB) has a compact helical crystalline conformation and a similar T_m , close to 180 °C, focused attention on fiber and packaging applications (Holmes, 1985). A summary time chart of technical developments reported for Poly(3HB) over the past 75 years is shown in Table 2.

Because it is a chiral linear polymer, Poly(3HB) can be a highly crystalline material. Lemoigne (see Bréchet and Desvaux, 1967) noted this feature in his early studies as he isolated Poly(3HB) samples of varying molecular weight resulting from autolysis of the microbial culture (Lemoigne, 1926, 1927). These variations in solubility and T_m of Poly(3HB) samples as a function of molecular weight were an important line of research for 25 years in the Lemoigne school (Kepes and Péaud-Lenoël, 1952). Maurice Lemoigne (see Biography) was a regular contributor to the scientific literature, including 27 papers on Poly(3HB)

Tab. 2 Time chart of bacterial PHA development and applications

	Extraction/Process	Observation	Application/properties
1920–1930	Solvent 20% HCl	Granules 157° melting point Optical rotation	Autolysis Fractionation Film-forming
1940	Solvent Crystallization	Chemical structure proof Melting point Saponification number	Crystalline powder Oligomers Cellophane-like
1960	Granule isolation Controlled extraction	Biocompatible Thermoplastic Colloidal granule suspension	Suture/coating Crotonic acid Packaging
1970	Enzymatic processing	Copolyesters Mechanical properties Molecular diversity	Plastics Drug delivery Chiral synthons
1980	<i>In vitro</i> synthesis Co-feeding	Cloning Thermal elastomer Functional sidechain	Commodity plastics Speciality plastics Biomedical uses
1990	Transgenic plants Co-feeding	Genetic engineering Seed selective biosynthesis Elastomeric properties	Degradable rubber Degradeable adhesive Adhesives

starting in 1923 until 1951. Many of his Poly(3HB) publications appeared in *C. R. Acad. Sci. and Ann. Inst. Pasteur*.

The history of Poly(3HB) development is significant in terms of polymer chemistry. Lemoigne (1923) found large amounts of poly(β -hydroxybutyric acid), (44% on bacteria dry weight) in cultures of *Bacillus megaterium* undergoing autohydrolysis. He traced this to refractile granules, insoluble in ether, which he named “lipide β -hydroxybutyrique”. He proceeded to demonstrate in the mid-1920s that these were linear polyesters which crystallized and could yield a series of oligomeric crystalline homologues – all this at a time when Staudinger was attacked by his German colleagues for proposing the existence of linear macromolecules (Morris, 1986). Clearly, organic chemists influenced by Emil Fischer did not have the paranoia of physical and colloid chemists who resisted

the idea. A summary of Maurice Lemoigne’s early Poly(3HB) experiments is shown in the box below.

Its β -substituted structure makes Poly(3HB) thermally unstable at temperatures immediately above the T_m due to the β -elimination reaction (see below). This characteristic suggested potential shortcomings as regards plastics and fiber applications. Baptist and Werber (1963) described molding, physical properties, and methods for production (Baptist, 1962a) and isolation (Baptist, 1962a,b) of the polymer, the latter process based on solvent extraction. One of the possible Poly(3HB) uses mentioned (Baptist, 1962a,b) was as an absorbable suture, i.e. a replacement for the venerable “cat gut”. The development (Lowe, 1954; Schmitt, 1967) of synthetic *absorbable* sutures based on copolymers of glycolic and lactic acids encouraged development work

Maurice Lemoigne Poly(3HB) Scientific Observations

Poly(3HB) is mentioned in 27 publications by Lemoigne from 1923 to 1951. His maximum yield of PHB from *B. megaterium* was 44% using glucose as substrate. It was reported as a polymer from condensation/polymerization of β -hydroxybutyric acid and identified as an optically active aliphatic polyester. This was in 1923 and it was the first literature mention of Poly(3HB).

He went on to study the bacterial inclusion which generated the polyester:

- CHCl_3 extraction $\xrightarrow{\Delta}$ collodion – like polymer film ($T_m=157^\circ\text{C}$)
- CHCl_3 extraction $\xrightarrow{\text{Ether}}$ white powder
- Bacterial mass $\xrightarrow[\text{extraction at the boil}]{\text{C}_2\text{H}_5\text{OH}}$ $\xrightarrow[3 \text{ min}]{20\% \text{ HCl}}$ $\xrightarrow[\text{CHCl}_3]{\text{boiling}}$ yield is 17–19% by weight ($T_m=157^\circ\text{C}$)
- Prepared oligomers with increasing melting point of 115, 120, 135 and 137 $^\circ\text{C}$, but all have the same saponification index, meaning they all have the same repeating unit. These were products of autolysis.
- Named them “lipides β -hydroxybutyriques”.
- After examination of various bacteria, he concluded that they all produced the same Poly(3HB) and that it was widely distributed in the soil.
- Mentions 40–60% yield on dry weight of bacteria in several publications.

on Poly(3HB) for potential prosthesis applications (Grace and Co., 1960) and other biomedical uses where slower absorption was desirable. Since *R*-(-)-3-hydroxybutyric acid is found in human blood, PHA has always been referred to as a biocompatible polymer.

A breakthrough in the potential commercialization of Poly(3HB) was the development by ICI of a family of copolyesters (Holmes, 1981; Holmes et al., 1981a,b; Holmes and Lim, 1985). Based on *Ralstonia eutropha* (formerly *Alcaligenes eutrophus*), these random copolymers, referred to in this chapter as Poly(3HB-co-3HV), had properties that could be tailored to fit a wide range of material needs. As the biosynthetic pathways became better understood, the importance of oxygen and phosphorous starvation rather than nitrogen limitation in the growth medium made possible the attainment of yields of Poly(3HB-co-3HV) as high as 85–90% based on the dry weight of bacteria. This development was the result of the biotechnology and environmental thrust of the 1970s.

Reliable analytical techniques eventually showed that different 3-hydroxyacid constituents were present in natural polyalkanoates from various bacteria (Wallen and Rohwedder, 1974). This eventually led to understanding the conditions when the naturally occurring storage granule is a homopolymer. However, it was the definitive demonstration by Wallen and Rohwedder (1974), that PHA with structures other than Poly(3HB) were present in estuarine sediments and sewage sludge, that alerted microbiologists to the compositional breadth of the PHA family.

Later, the so-called medium-chain-length (MCL)-PHA were discovered as the product of *Pseudomonas oleovorans* feeding on hydrocarbons or fatty acids. These polymers with side chains of five carbons or more had distinctly different physical properties – they

were thermoplastic elastomers (De Smet et al., 1983; Brandl et al., 1988). Steinbüchel and Valentin (1995) have catalogued over 90 different PHA structures, all naturally occurring.

While ICI was developing the Poly(3HB-co-3HV), Biopol™, Lafferty and Braunegg (1988) found advantages in using a strain of *Alcaligenes latus* for commercial production of Poly(3HB). For a few years in the late 1980s Chemie Linz in Austria supplied Poly(3HB) from a (40 tons per year) pilot operation which used solvent extraction and recovery to isolate the polymer.

3 General Use Properties

Poly(3HB) homopolymer is a thermoplastic material, meaning that it is a resin that becomes highly viscous and moldable at temperatures close to or above the T_m . Its properties are often compared to those of polypropylene, as both polymers have T_m s, degrees of crystallinity, and glass transition temperatures (T_g s). However, Poly(3HB) is both stiffer and more brittle than polypropylene. The brittleness of Poly(3HB) is largely due to the presence of large crystalline domains in the form of spherulites, which form upon cooling from the melt; suitable processing conditions can reduce the brittle character, allowing production of ductile films (Barham and Keller, 1986). The materials also differ in chemical properties, with Poly(3HB) having a lower solvent resistance but much better natural resistance to ultraviolet weathering than polypropylene. Early evaluations of Poly(3HB) included the production of a number of moldings, extrudates, films, and fibers (Holmes, 1985; Holmes and Lim, 1985). The properties of these materials were generally satisfactory, but not spectacular.

Packaging film had excellent gas barrier properties, being 5 times less permeable to CO₂ than was poly(ethylene terephthalate) (PET) and was as strong as polypropylene film, but not as tough as PET. Poly(3HB) can be strengthened by addition of a glass fiber filling (King, 1982); glass-reinforced moldings were stiffer and tougher than similar nylon parts.

Properties are greatly improved in the Poly(3HB-co-3HV) bacterial copolymers. With increasing concentrations of 3HV units from 0 to 25%, there is a decrease in T_m (Table 3), increasing the size of the processing window within which the polymer can be melted without being degraded.

The T_g also decreases, allowing use of these materials at lower temperatures without embrittlement behavior. The steady decrease in Young's modulus (also known as the flexural modulus) indicates improved flexibility. The notched Izod impact strength also increases with increasing 3HV concentration, indicating that the toughness of the material is increasing. The biosynthetic origin of Poly(3HB-co-3HV) copolymers adds a number of interesting properties to these materials, relative to purely synthetic polymers. Having been made by bacteria as a carbon reserve, these materials can also be degraded by bacteria, putting them amongst the few fully biodegradable, thermoplastic materials.

Another result of its biosynthetic origins is optical activity (Marchessault et al., 1970; Akita et al., 1976), meaning that films or solutions of Poly(3HB-co-3HV) will rotate the plane of polarized light passing through them. This arises because the β -carbon in every monomer in a Poly(3HB) or Poly(3HB-co-3HV) chain has an *R* absolute configuration; thus, the polymer is chiral which leads to a high level of crystallinity when appropriate casting or molding conditions are used. Furthermore, these crystals have no center of symmetry, causing a change in direction of average dipole moment if the crystals are deformed in a particular way (Fukada and Ando, 1986). This produces a polarization such that a surface charge is generated in response to deformation in shear modes; in short, the material generates a voltage when squeezed or deforms when a voltage is applied to it (Fukada and Ando, 1986). This property is known as piezoelectricity and is typical of many biological systems, but not usually of plastics.

The importance of the ICI copolyester family of products (Table 3), marketed under the trade name Biopol, was to show that bacterial polyesters could be manufactured with a range of properties (e.g. T_m , toughness, flexibility, etc.). No one doubted that large-scale fermentation production of PHA was possible, but the enzyme-based biotech purification method (Holmes, 1985;

Tab. 3 Physical properties of Poly(HB-co-HV) copolymers (Holmes, 1987)

<i>Poly(HB-co-HV)</i> (mol% HV)	T_m (°C)	T_g (°C)	<i>Young's</i> <i>modulus (GPa)</i>	<i>Tensile</i> <i>strength (MPa)</i>	<i>Notched Izod impact</i> <i>strength (J m⁻¹)^a</i>
0	179	10	3.5	40	50
3	170	8	209	38	60
9	162	6	1.9	37	95
14	150	4	1.5	35	120
20	145	-1	1.2	32	200
25	137	-6	0.7	30	400

^a With 1-mm radius notch.

Holmes and Lim, 1985), replacing the solvent extraction approach, is what caught the attention. In addition, Poly(3HB-*co*-3HV) displayed unusual properties, i.e. high crystallinity at all compositions. This differs from the usual case where the random addition of a comonomer to a crystallizable homopolymer results in a drop in the T_m followed by a complete loss of crystallinity, at about 15 mol%. In the case of Poly(3HB-*co*-3HV), the T_m versus mol% 3HV curve displays a pseudo-eutectic point between 35 and 40% 3HV (Figure 1). On one side of the pseudo-eutectic the Poly(3HB) lattice is the sole crystalline phase, while the Poly(3HV) lattice is found on the other side. Since nuclear magnetic resonance (NMR) analysis shows that the comonomer sequence distri-

bution of Poly(3HB-*co*-3HV) is Bernoullian (Doi et al., 1986a,b), while the degree of crystallinity is 60% or more at all compositions, one concludes that this crystalline system is isodimorphic (Bluhm et al., 1986). This term implies co-crystallization, i.e. the Poly(3HB) lattice accommodates 3HV comonomer units and vice versa. While this is a rare occurrence in copolymers, the Poly(3H β -*co*-3HV) system does satisfy the necessary conditions for isodimorphism (Allegra and Bassi, 1969), similarity of monomer size, and similarity of crystalline conformation (see below). Figure 1 includes experimental data from bacterial and synthetic copolymers which give a poorly defined eutectic point. However, the isodimorphism phenomenon has been confirmed by several studies (Mitomo et al., 1993) for bacterial Poly(3HB-*co*-3HV).

When isodimorphism was examined for melt-crystallized systems (Bluhm et al., 1986) (Figure 1) the a parameter of the unit cell was found to undergo a small linear change with the percentage 3HV up to the transition composition where the Poly(3HB) phase changed to Poly(3HV) and from there on it remained constant. On the basis of the lattice change, while crystallinity remained constant, it has been argued that a non-equilibrium state is involved. Thus, if the partitioning of 3HV units between the crystalline and non-crystalline domains depends on crystallization temperature and the crystal 3HV content is always smaller than the average chain, then a kinetic mechanism is operative (Barker et al., 1997). Furthermore, experiments support the fact that the amount of 3HV in the crystals decreases with increasing crystallization temperature (Barham et al., 1992). The latter is best explained in terms of kinetic energy available to find favorable packing arrangements. Several studies have been reported of solid-state NMR (^{13}C -cross-polarization magi-

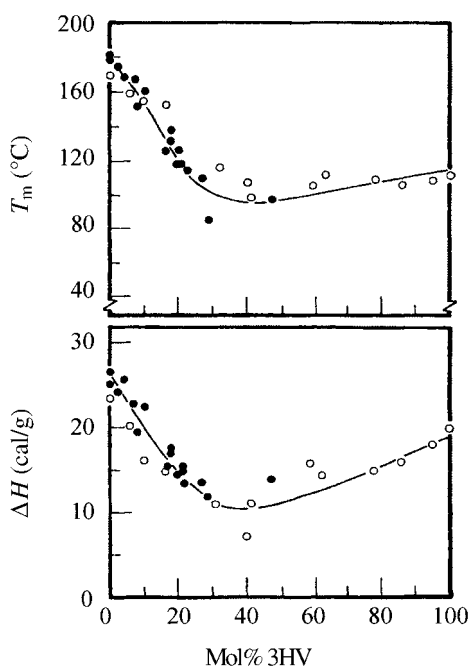


Fig. 1 Variation of melting point (T_m) and enthalpy of fusion (ΔH_f) with composition of bacterial (solid circles) and fractionated synthetic (open circles) Poly(3HB) (redrawn and adapted from Bloembergen et al., 1986).