

CCA-1714

YU ISSN 0011-1643

UDC 547+541.64

Original Scientific Paper

Influence of the Stereochemical Structure on The Physicochemical Properties of Polymers Prepared by Ring-Opening Polymerization of Chiral Heterocyclic Monomers

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Received June 27, 1986

Physico-chemical properties of polymers prepared by ring-opening polymerization of heterocyclic chiral monomers with different enantiomeric composition are compared. Two general kinds of behaviour were observed for products with a mono-substituted carbon in the chain: when the substituent group is not bulky the properties of polyenantiomers and their racemic mixture are very similar; when the substituent is a bulky group, e.g. *t*-butyl, many of the properties (m. p., crystalline structure, solubility, etc.) are very different for the same polymers. The corresponding statistical stereocopolymers are amorphous. For polymers with disubstituted asymmetric carbon atoms the statistical stereocopolymers are crystalline and their melting behaviour varies with the enantiomeric purity. In some cases a strong dependence of the mechanical and biological properties on the enantiomeric purity of stereocopolymers is reported.

I — INTRODUCTION

The ring-opening polymerization of heterocyclic compounds containing one asymmetric center in the ring leads to macromolecular chains having a wide variety of structural arrangements. The following distribution of enantiomeric units, described as R and S may be found:

Structure

- | | |
|---------------------|----------------------------|
| (1) — RRSRSSRS — | random copolymer |
| (2) — RSRSRSR — | alternate copolymer |
| (3) — RRRRRRRR — | polyenantiomer |
| (4) — RRRR ~ SSSS — | block copolymer |
| (5) — RRRRRRRR — | |
| + | mixture of polyenantiomers |
| — SSSSSSSS — | |

Structure of type (2), i. e. alternate (syndiotactic) copolymer, has not yet been prepared in a pure form by ring-opening polymerization. Block copolymers (4) have not been studied to a large extent and require special preparation techniques, such as living-type polymerizations.

Most of the studies have been devoted to polymers of type (1), (3) or (5), the last being usually prepared by stereospecific polymerization of the racemic monomer and much more rarely by an artificial mixture of the two enantiomeric chains.

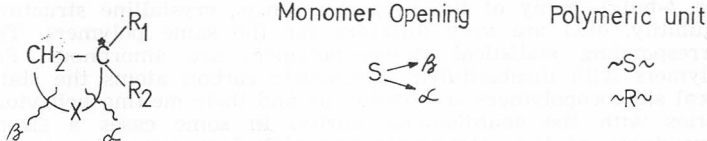
Physico-chemical properties may strongly depend upon the enantiomeric composition of the polymer chain. Such changes in the properties have been mainly described in two series of products: those in which the macromolecular chain is continuously enantiomerically enriched passing from type (1) to type (3) and those in which unbalanced mixtures of enantiomeric chains are compared i. e. gradual evolution from type (3) to type (5).

In this paper we examine some examples taken from the literature and from our own works related to studies on the properties in solid state and in solution of the polymer series cited above.

Some indications are given on the determination of structure by NMR and X-ray methods. In the first part of the paper we summarize some synthetic methods allowing the preparation of different types and families of polymers.

II — SYNTHESIS OF POLYMERIC CHAINS WITH VARIOUS ENANTIOMERIC DISTRIBUTIONS

Heterocyclic monomers are usually polymerized with ionic type initiators. The ring-opening reaction may involve (α) or not involve (β) the asymmetric centre.



In the case of α -scission the configuration of the asymmetric carbon is generally inverted during the ring-opening reaction¹; therefore, an S-type enantiomer leads to an R-type enantiomeric unit in the chain. Such a process, which is frequent in cationic polymerizations of three-membered ring heterocycles, introduces irregularities, e. g. head-to-head units, in the macromolecular chain and should be avoided.

We shall therefore consider, when possible, only synthetic methods in which the asymmetric centre is not involved and chains with regular structure are formed.

2.1. POLYMERS WITH BOTH ENANTIOMERIC UNITS IN THE SAME MACROMOLECULAR CHAIN

In order to obtain a polymer with a given enantiomeric composition $R/S = m/n$, one may start from a monomer mixture of the same composition and proceed to a polymerization without involving the asymmetric centre during the ring-opening reaction as stated above.

In general, anionic initiators are convenient for such preparations and cationic initiators must be avoided. Moreover, if one wants to have a polymer with statistical distribution of enantiomeric units in the polymer chain, one must avoid the use of stereospecific, e. g. anionic-coordinated, initiators.

The following families of heterocyclic compounds have been polymerized and the properties of their products with different enantiomeric content studied as described later on.

Thiiranes

Thiiranes may be polymerized using different organometallic compounds or pure alkaline metals as initiators. For example, racemic and optically active poly methyl, isopropyl, *t*-butyl thiiranes were obtained by simply polymerizing the corresponding monomers on sodium mirrors.² One must be aware that with some organometallic compounds, such as butyl lithium and complexes with lithium alkoxides, elimination reactions may occur leading to the formation of polysulfide linkages and irregular structures.³

Oxiranes

Optically active poly(propylene oxide) was the first stereoregular polymer prepared from the corresponding cyclic optically active monomer.⁴ The polymer prepared with KOH was of l.m.w. but shows a melting point. The corresponding product prepared from the racemic monomer was amorphous. The polymerization of propylene oxide with anionic initiators is accompanied by the formation of unsaturated type products due to secondary reactions⁵ and h.m.w. products with statistical distributions cannot be obtained using these initiators. Recently, a tetraphenylporphyrin — AlEt_2Cl initiator system was described⁶ allowing the preparation of poly(propylene oxide) of desired molecular weight with no termination reaction. Optically active polymers and oligomers can be prepared by this system.⁷ For highly substituted oxiranes, e.g. *t*-butyloxirane, initiator systems such as *t*BuOK in bulk or in DMSO solution were applied.⁹⁻¹⁰ In bulk stereoelective effects may be observed⁹: the enantiomeric composition of the resulting polymer at partial conversion is different from that of the starting monomer. The same type of effect was observed in the case of styrene oxide.¹¹ The stereoelective effect is due to the complexation of the cation K^+ by the ethereal chain end and it can be suppressed by the addition of complexing agents such as crown-ethers or cryptands.¹¹

Lactones

α,α -disubstituted β -propiolactones are easily polymerized using carboxylic acid salts, e.g. tetraalkylammonium benzoate,¹² or potassium acetate activated with crown-ether.¹³ β -substituted β -propiolactones are not polymerized by anionic initiators. Aluminium¹⁴ and zinc¹⁵ modified coordination type initiators were used in the case of β -butyrolactone and also in the case of highly β -substituted β -propiolactones.¹⁶ A living type polymerization was described more recently using AlEt_2Cl -tetraphenylporphyrin initiator system¹⁷ and a series of optically active polyesters was prepared from different β -propiolactones using this system and also initiators derived from zinc and aluminium alkyls.¹⁸

Oxetanes

α -Substituted oxetanes are not polymerizable by classical anionic initiators. Cationic initiators, such as carbonium salts, or coordinated initiators, such as $\text{AlEt}_3/\text{H}_2\text{O}/\text{Acetylacetone}$, must be used.¹⁹

Lactides

The synthesis of poly(α -hydroxyacid)'s(poly lactides) involves the polymerization of lactide cyclic diesters. The lactide exists as: RR and SS antipodes, RS isomer and RR + SS solid compound (racemic). When using an initiator which does not change the configuration, poly lactides of desired configuration can be obtained. Different initiators, such as various cationic ones,²⁰ powdered zinc, SbF_3 ,²¹ tetraphenyltin²² etc., were used. The stereosequence distribution in the polymer chain is perturbed by transesterification reactions, as shown by NMR studies²³.

Lactams

The statistical copolymer of the two enantiomers and the optically active poly(β -propiolactam)'s were obtained by anionic polymerization (KOH or pyrrolidone potassium salt in DMSO) of the racemic and optically active monomers, respectively.²⁴

Thiolactones

Optically active R(+) 2-methyl-2-ethyl-3-propiothirolactone has been synthesized and polymerized using tetrabutylammonium versatate as initiator.²⁵

2.2. POLYMERS CONSTITUTED OF MIXTURES OF TWO ENANTIOMERIC CHAINS

The most obvious and rigorous way of preparing such polymers is to make a synthetic mixture of the two polyenantiomeric chains with opposite configuration prepared by the synthetic methods described above.

The preparation of pure enantiomers is, however, a long and difficult operation. Therefore, when possible, this method is avoided. Indeed, mixtures of polyenantiomeric chains can be obtained by stereospecific polymerization of the racemic monomer using zinc, cadmium and aluminium modified initiators. The last ones can be chiral or achiral depending on the desired final products. The selectivity of such initiators is often only partial and, therefore, in addition to crystalline isotactic polymer, some amount of amorphous fraction is obtained. In the case of polyoxiranes and polylactones this amorphous fraction can be separated by selective solvent extraction. Stereospecific polymerizations with chiral and achiral initiators have been already described in detail in the literature.^{26,27}

An interesting result was reported in the polymerization in the solid phase on irradiation of β -chloroalkyl β -propiolactones.²⁸ According to the crystal structure analysis determined by X-rays, the poly(β -trichloromethyl β -propiolactone) prepared by this procedure was isotactic forming a racemic lattice. Unfortunately, due to complete insolubility of these products, the stereoregularity of the polymer chains could not be determined.

III — DETERMINATION OF THE STRUCTURE OF MACROMOLECULAR CHAIN BY NMR

In order to compare the properties of different polymers it is obviously necessary to know the distribution of enantiomeric units in the macromolecular chain. Chiroptical properties can give the relative ratio of S and R units in the polymer but they are unable to give the way of distribution of these

enantiomeric units. The method for such a determination is NMR. Both ^1H and ^{13}C NMR were used. Bernoullian triad distribution was established and correlated by ^1H 300 MHz NMR for deuterated poly(propylene sulfide)'s prepared by anionic way.²⁹ The fitting with bernoullian tetrad distribution was confirmed by 100 MHz ^{13}C and 500 MHz ^1H NMR for poly(α -methyl α -ethyl β -propiolactone)'s of different enantiomeric purities prepared by anionic initiators.³⁰ It was also established by comparison with the spectra of optically pure polymers that polymers prepared by stereospecific initiators are isotactic. Redistributions of stereosequences occurring by transesterification at the ester bonds in the melt were discussed in the case of poly(lactic acid).²³ Finally, with aluminium initiators, a non bernoullian distribution was found in the case of 2-methyl oxetane.¹⁹ With other aluminium initiators, markovian type distributions are under study in the case of poly(methyl oxirane)'s.³¹

IV — PROPERTIES OF MATERIALS

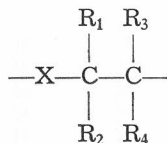
Materials with various enantiomeric compositions and different crystalline structures prepared by the methods described above show differences in the properties in the solid state and in solution.

Melting points, crystallization and mechanical properties were examined on solid materials, while solubility, chiroptical and hydrodynamic properties were studied on materials in solution.

4.1. PROPERTIES IN SOLID STATE

4.1.1. Melting Behaviour

In Table I some typical examples of polymers are given having the following general configurational unit:



where X can be S (thiirane); O (oxirane); OCH_2 (oxetane) $-\text{OC}-$ (α -substi-

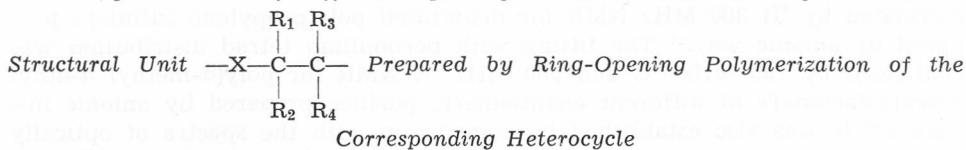
tuted β -propiolactone); $-\text{C}-\text{O}-$ (β -substituted β -propiolactone); $\text{NHC}-$ (lac-

tam); $-\text{S}-\text{C}-$ (thiolactone).

The melting behaviour of polymers depends on the different distribution of enantiomeric units in the chain, i. e. random polymer ($-\text{RRS}-$) or pure poly enantiomer ($-\text{RRR}-$), as well as for the racemic mixture of enantiomeric chains ($-\text{RRR}- + -\text{SSS}-$). A classification may be based on the comparison of the similarities or differences in properties between these 3 types of polymers and two main classes of products can be identified.

TABLE I

Melting Behaviour of Different Optically Active and Inactive Polymers with



X	R ₁	R ₂	R ₃	R ₄	Melting point T _m (°C)			Ref.	
					Statist. $\begin{array}{l} \sim \\ \text{RRS} \\ \sim \end{array}$	Enant. $\begin{array}{l} \sim \\ \text{RRR} \\ \sim \end{array}$	Rac. mix $\begin{array}{l} \sim \\ \text{RRR} \\ \sim + \text{SSS} \\ \sim \end{array}$		
-S-	Me	H	H	H	am	63	62	32	
	Et	H	H	H	am	58	62	35	
	iPr	H	H	H	am	am	160	44	
	nBu	H	H	H	am	—	57/68	35	
	tBu	H	H	H	H	am	160	205	33
	Me	Et	H	H	H	111	—	128/161	34, 35
-O-	Me	H	H	H	am	72	72	4	
	iPr	H	H	H	am	53	—	45	
	tBu	H	H	H	am	147	150	10, 36	
	Me	Et	H	H	101	—	110	37	
-O-CH ₂	H	H	Me	H	am	am	—	19	
-O-C(=O)-	Me	Et	H	H	122	164	192	13	
	Me	nPr	H	H	80	—	—	64	
	Me	iPr	H	H	25	—	—	64	
	Et	nPr	H	H	205	—	—	64	
	Et	nBu	H	H	180	—	—	64	
	Et	Ph	H	H	115	239	—	38, 49	
	Et	Bz	H	H	147	222	—	49	
	H	H	Me	H	am	180	170—175	14, 39, 48	
	H	H	Et	H	am	—	105—108	61	
	H	H	iPr	H	am	—	72—79	43	
	H	H	CH ₂ Cl	H	am	—	140—146	43	
	H	H	CHCl ₂	H	am	—	138—146	43	
	H	H	CCl ₃	H	am	256	—	18	
	H	H	CH ₃ CCl ₂	H	am	164	—	42	
	H	H	C ₂ H ₅ CCl ₂	H	am	145	—	42	
H	H	C ₃ H ₇ CCl ₂	H	am	120	—	42		
H	H	CF ₃	CH ₃	am	100—110	—	18		
-NH-C(=O)-	H	H	Me	H	328	345	n. d.	24	
	H	H	Et	H	330	380	—	24	
	Me	Et	H	H	76	—	—	65	
	Me	iPr	H	H	74	—	—	65	
	Me	nBu	H	H	72	—	—	65	
	Et	Ph	H	H	am	298	—	50	

$-(\text{CH}_2)_3-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-$	H	H	Me	H	145	225	—	62
$-\text{S}-\overset{\text{O}}{\parallel}{\text{C}}-$	Me	Et	H	H	260	260	—	25
$-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{R}_3}{\text{C}}-$ (lactide)			Me	H	am	173	—	23
			iPr	H	am	~195	—	63
			iBu	H	am	am	—	63

(am) amorphous; (n. d.) not determined; (—) not available.

A-Materials for which the polyenantiomer and the racemic mixture of enantiomeric chains have similar properties and identical crystalline structures. This is the case, for example, of poly(propylene oxide), poly(propylene sulfide), poly(hydroxybutyrate), etc. Usually, the corresponding statistical copolymers are not crystalline.

B-Materials for which the polyenantiomer and the racemic mixture have very different properties and different crystalline structures. This class is well illustrated by poly(*t*-butyl-thiirane), (PTBT) for which a difference of 45 °C between the m. p. of poly S and (poly R + poly S) polymers was found. Another example is poly (α -methyl α -ethyl β -propiolactone) (PMEPL) for which a $\Delta T_{mp} \sim 30$ °C between the two products exists. However, the statistical copolymer of the two enantiomers of TBT is amorphous, while the corresponding PMEPL is crystalline.

Studies of crystalline structures of PMEPL have not yet been completed but it appears that the enantiomeric (poly S) and the statistical poly (R, S) polymers have the same structure, with some distortion in the lattice for the latter, while the racemic polymer (poly R + poly S) has a different structure^{13,40,41}, as in the case of PTBT⁴⁶.

There are still many polymers which have not been prepared in the three forms or/and the properties of which have not been completely studied and particularly the crystalline structure not yet determined.

Some polymers do not completely fit into this classification.

For example, poly(isopropylthiirane)⁴⁴ and poly(2-methyloxetane)¹⁹ are not crystalline in the optically active form. Other polymers are known to be crystalline in their random and racemic forms, e. g. poly(Me, Et oxirane) and poly(Me, Et thiirane), but their polyenantiomers have not been prepared yet. Monosubstituted poly(β -lactam)'s have a particular behaviour. It was reported that statistical and enantiomeric poly(β -butyrolactam)'s have different m. p. and different crystalline structures²⁴. The polymer obtained by mixing poly R and poly S chains seems to have the same structure as the polyenantiomers, although its m. p. was not indicated. However, the oriented samples showed the same X-rays diagrams. Poly D- and poly(D,L- β -methyl- ϵ -caprolactam)'s showed also a great difference in their m. p. but the crystalline structure was not established⁶².

From the data in Table I it appears as a general trend that polymers in which one of the substituents of the asymmetric carbon atom is hydrogen do not show any crystallinity when they are random stereocopolymers with R and S units. On the other hand, polymers with disubstituted asymmetric carbons such as methyl, ethyl — poly oxiranes, thiiranes, β -propiolactones, β -propiothirolactones and others produce crystalline products with statistical distribution of configurational units in the chain, as established by NMR. In the series of α, α' disubstituted poly(β -propiolactone)'s it was observed that the m. p. decreases with the ratio of carbon atom numbers in substituents R_2/R_1 on the asymmetric centre¹².

Poly lactams seem to be an exception to this rule, most of the monosubstituted products being crystalline, but such behaviour can be caused by particular interactions which are known to be present in the polyamids.

Interesting information on the change of properties can be obtained following the behaviour of materials which are stepwise enantiomerically enriched. Such studies were mainly performed on polythiiranes, poly(β -propiolactone)'s and polylactides. The variation of melting points and enthalpies in the function of enantiomeric purity is illustrated in Figure 1. In the case of PMEPL the m. p. does not change markedly up to enantiomeric excess: e. e. = 50%, then it increases linearly¹³. For PTBT, the random copolymer is amorphous and the crystallization appears only for chains with e. e. > 80%⁴⁷. A Raoult type correlation was established between the depression of m. p. and the enantiomeric composition⁴⁷. The behaviour of polylactide is similar to the previous one: polymers with a L-content lower than 87.5% are amorphous²³.

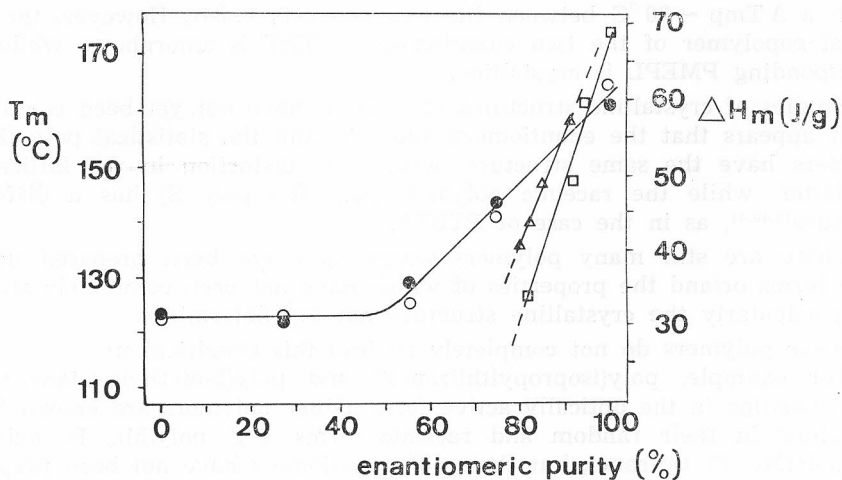


Figure 1. Variation of melting points of polymers prepared from monosubstituted and disubstituted chiral heterocyclic monomers versus their enantiomeric purity. Melting point T_m (°C).

- poly (lactide) (ref. 21)
- △ poly (*t*-butyl thiirane) (ref. 47)
- poly (α -methyl- α -ethyl- β -propiolactone) (ref. 13) Enthalpy ΔH_m (°C).
- poly (α -methyl- α -ethyl- β -propiolactone) (ref. 13)

It is worth mentioning that such studies are valid when they are performed on polymers with comparable molecular weights ($>20,000$). Indeed, it is known that for l. m. w. polymers the m. p. could vary dramatically with the m. w., as it was demonstrated in the case of poly(*t*-butyloxirane)^{9,10} or PHB⁴⁸, for example.

4.1.2. Crystallization Properties. Morphology

Few studies on crystallization and morphology have been performed on both optically active and racemic polymers. Kinetics of spherulite crystallization has been studied on racemic ($M_n = 135,000$) and optically active ($M_n = 10,300$) poly(propylene oxide)'s⁵¹ prepared by unspecified but probably two different types of initiators. Both polymers have similar physical properties except that the racemic one usually gives the non-ringed spherulites while the enantiomeric one exhibits, ringed type. Poly(epichlorhydrin)'s of different stereoregularities were compared, some of them being enantiomerically enriched (prepared by stereoselective type initiators)⁵². Two types of spherulites negatively birefringent were observed. Polymers having the highest optical rotations crystallize faster and in the form of type II spherulites. Crystallization and morphology of bacterial PHB crystals were studied in detail⁵³ but have not yet been compared to that of the synthetic racemic polymer. Systematic studies were performed on poly(α -methyl α -ethyl β -propiolactone)'s. It was shown that the growth rate significantly increases with the enantiomeric purity⁴⁰. The polymer crystal growth follows regime II in which a large number of surface nuclei form on the crystal, while their lateral growth is slow. The average radii of the spherulites were measured from small-angle light scattering and it appears that the statistical copolymer has radii of about 30 μm , while the almost enantiomerically pure one has a radius close to 4 μm . Binary mixtures of poly R and poly S isotactic PMEPL were then studied.⁴¹

The racemic mixture PMEPL 50S—50R which exhibits a much higher m. p. (202 °C) than the polyenantiomer one (164 °C) shows also a much larger spherulite radius (close to 500 μm). In binary mixtures the rate of crystallization of the racemate is much greater than that of the polyenantiomer one and, therefore, even in enantiomeric composition of 97S—3R the spherulites of the racemate stereo complex predominate. In another study on poly(α -methyl- α -*n*-propyl β -propiolactone)'s polymers prepared in the presence of homogeneous and heterogeneous initiators were compared⁵⁴.

Polymers prepared in the heterogeneous way crystallize much faster than those prepared with homogeneous initiators, but the former give a disordered morphology. No highly enantiomerically enriched polymers were available allowing comparison of these properties with those of the racemic one.

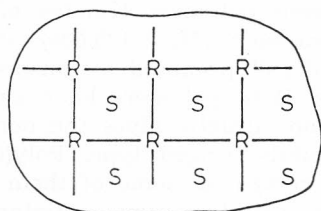
The general crystallization behaviour of poly(L-lactic acid) was studied⁶⁷ and the various nucleation parameters were calculated⁶⁸.

4.1.3. Crystalline Structure and Modes of Optical Activity Compensation in Racemic Polymers

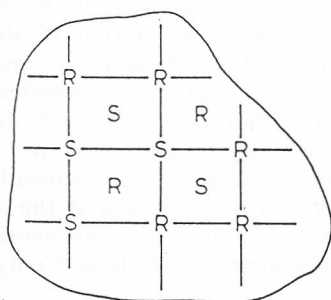
The crystalline structure of many polymers prepared by ring-opening polymerization has been determined and information on crystal systems, molecular conformations, crystal densities is available in specialized review^{55,56}.

The structure and the optical activity compensation of polymers having asymmetric carbon atoms in the main chain were discussed only in a few cases.

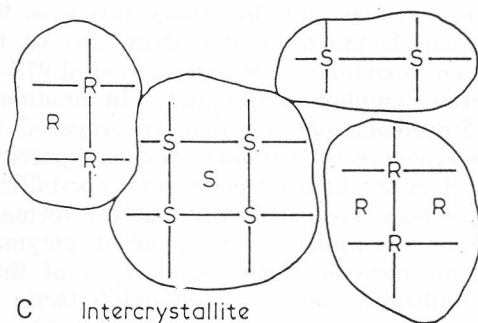
When R and S isotactic polymers are mixed in a 1:1 ratio, three kinds of optical activity compensation can be considered⁵⁷ (Figure 2): (a) The optical isomeric chains are included in the unit cell pairwise giving an optical activity compensation in a unit cell i. e. a racemic lattice (b) The isomeric polymers are included in the crystallite randomly forming a statistical disordered structure and the compensation is in the crystallite (c). Each crystallite is



a Racemic lattice



b Intracrystallite



c Intercrystallite

Figure 2. Methods of optical compensation of racemic polymers.

(From ref. 56).

(a) Compensation in a unit cell,

(b) Compensation in a crystallite,

(c) Intercrystallite compensation.

R and S are, respectively, rectus and sinister chains.

formed only of R polymers and only of S polymers. As there are equal amounts of enantiomeric crystallites, the bulk polymer is optically inactive giving an intercrystallite compensation.

In case (c) the optically active and the racemic polymer (poly R/poly S = 1 : 1 mixture) have the same crystalline structure and the same physical properties (m. p., density, solubility). In case (a) the racemic polymer has a crystalline system different from that of the enantiomeric one and different physical properties, e. g. different melting points, as discussed in the preceding chapter.

Some crystallographic data of known optically active and racemic polymers are given in Table II.

TABLE II

Crystallographic Data for Some Racemic (rac.) and Optically Active (o. a.) Polymers and Methods of Optical Compensation of Racemic Isotactic Polymers

Structural unit	Crystal system	Space group	Molecular conform.	Optical compensation	Ref.
$\begin{array}{c} \text{---O---CH---CH}_2\text{---} \\ \\ \text{Me} \end{array}$	Orthorhomb. rac. and o. a.	$P2_1 2_1 2_1$	dist. planar zigzag (2/1)	(b) or (c)	58
$\begin{array}{c} \text{---O---CH---CH}_2\text{---} \\ \\ \text{iPr} \end{array}$	Orthorhomb. o. a.	$P2_1 2_1 2_1$	helix (2/1)		45
$\begin{array}{c} \text{---O---CH---CH}_2\text{---} \\ \\ \text{tBu} \end{array}$	Tetragonal rac. o. a.	$P4 n_2$ $c=24.65 \text{ \AA}$ $c=11.05 \text{ \AA}$	helix (9/4)	(a)	57 59
$\begin{array}{c} \text{---S---CH---CH}_2\text{---} \\ \\ \text{Me} \end{array}$	Orthorhomb. rac. and o. a.	$P2_1 2_1 2_1$	dist. planar zigzag (2/1)	(c)	60
$\begin{array}{c} \text{---S---CH---CH}_2\text{---} \\ \\ \text{iPr} \end{array}$	Orthorhomb. o. a.	$I2cb$	dist. helix (2/1)		57
$\begin{array}{c} \text{---S---CH---CH}_2\text{---} \\ \\ \text{tBu} \end{array}$	rac.: Monoclinic o. a.: Trigonal	$P2_1/a$ $P3_1$	helix (3/1) helix (3/1)	(a)	46
$\begin{array}{c} \text{---O---C---CH}_2\text{---CH---} \\ \quad \\ \text{O} \quad \text{Me} \end{array}$	Orthorhomb. rac. and o. a.	$P2_1 2_1 2_1$	helix (2/1)	(c)	39
$\begin{array}{c} \text{---O---C---CH}_2\text{---CH---} \\ \quad \\ \text{O} \quad \text{Et} \end{array}$	Orthorhomb. rac.	$P2_1 2_1 2_1$	helix (2/1)	(c)	61
$\begin{array}{c} \text{Me} \\ \\ \text{---O---C---C---CH}_2\text{---} \\ \quad \\ \text{O} \quad \text{Et} \end{array}$	o. a.: Monoclinic rac.: different, n. d.	$P2_1 C_2^2$	helix (2/1)		40
$\begin{array}{c} \text{---NH---C---CH}_2\text{---CH---} \\ \quad \\ \text{O} \quad \text{Me} \end{array}$	Orthorhomb. rac.	$P2_1 2_1 2_1$			65
$\begin{array}{c} \text{---O---C---CH---} \\ \quad \\ \text{O} \quad \text{CH}_3 \end{array}$	Orthorhomb. Hexagonal		helix (10/3)		66 67

Much less information is presently available on polymers which are already crystalline in their statistical form. In the case of poly(α -methyl- α -ethyl- β -propiolactone) highly oriented films and fibers cannot be obtained in all cases and the structural analysis must be carried out on unoriented samples. It was established⁴⁰ that optically active and statistical PMEPL have the same monoclinic cell corresponding to $P2_1-C_2^2$ space group but the cell of the statistical copolymer is slightly distorted. The crystal structure of the racemic (poly R + poly S) sample is different from that of the enantiomeric one, but the space group has not yet been determined⁴¹. It is, therefore, possible that in this case again an optical activity compensation of type (a), i. e. racemic lattice, is present.

4.1.4. Mechanical and Biological Properties

Very little information is available on the comparison of mechanical properties of crystalline optically active, statistical and racemic polymers.

In the case of poly(α, α -disubstituted- β -propiolactone)'s some stress-strain curves were recorded. For example, low optical purity samples of PMEPL were highly deformable, while high optical purity samples show a fragile fracture at an elongation of about 4% before any yield point⁴⁰. All the samples have the same Young's modulus. The same observation was made in the case of poly(β -butyrolactam)'s²⁴. Interesting features were described in the case of lactic acid stereocopolymers. It was already mentioned that a strong decrease of m. p. with enantiomeric purity was observed²¹, i. e. when e. e. decreases from 100 to 81.5, the m. p. drops from 173°C to 124°C. Most of the tests on poly(lactic acid) polymers were related to biodegradation of implanted specimens^{21, 69}. The degradation rate increases as the enantiomeric purity of L-polymer decreases and only optically L-pure implants were not degraded histologically after 12 months, while all other stereocopolymers were resorbed.

The variation of tensile strength with implantation time was studied and it was observed that after 2 months, if the optically pure implant did not show any decrease in tensile strength, the polymer of e. e. = 84% lost approximately 20% of the initial σ_B , while the e. e. = 50% polymer lost all its stiffness (Figure 3). It was concluded that only materials with e. e. higher than 84% exhibit degradation rates low enough for orthopedic surgery.

V — PROPERTIES IN SOLUTION

5.1. SOLUBILITY

There are usually differences in solubility between statistical copolymers (atactic), which are often amorphous, and isotactic polymers (enantiomeric or racemic), which are usually crystalline. The latter are much less soluble. In some cases particularly with polyoxiranes, the isotactic polymer can be completely insoluble in one solvent, while the statistical polymer is soluble. For example, isotactic poly(propylene oxide) is insoluble in acetone and can be fractionated from the amorphous part. A similar fractionation can be used for polyhydroxybutyrate by insolubility in acetone⁴³ or in methanol¹⁵.

Selective solubility separation between the optically active polymer and the racemic one is much less frequent. However in, the case of poly(*t*-butylthiirane) the optically active polymer is soluble in toluene and in chloroform,

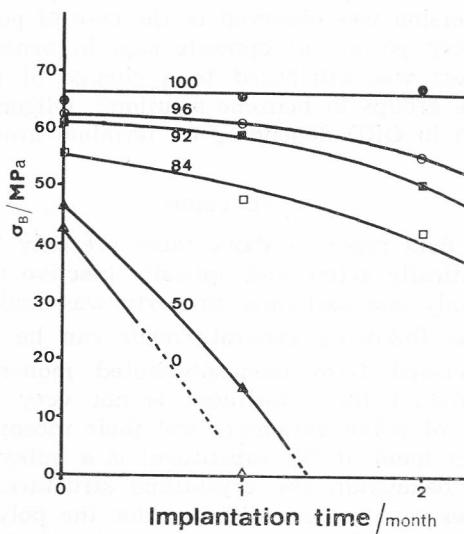


Figure 3. Variation of the tensile strength with time for stereocopolymers of lactic acid with various enantiomeric purities (100, 96, 92, 84, 50, 0) (from ref. 21).

while the racemic isotactic one is insoluble in toluene and hardly soluble in chloroform⁷⁰. Thus, the racemic stereocomplex can be separated from an enriched enantiomeric mixture. In the case of poly(α -methyl α -ethyl β -propiolactone)'s the polyenantiomer is insoluble in the usual solvents when its m. w. is higher than 5000. It can therefore, be separated from the statistical copolymer, but not differentiated from the racemate one which is also very insoluble.

5.2. CHIROPTICAL PROPERTIES

In principle, for all the polymers we have described the optical rotation varies linearly with the enantiomeric purity whether these polymers contain both enantiomeric units in the same chain or they are mixtures in different amounts of polyenantiomeric chains. This means that there are no conformational effects.

Therefore, for anionically prepared polymers the optical activity is a convenient tool for the measurement of the enantiomeric excess and it can be correlated with enantiomeric distribution obtained from NMR measurements^{2,29,30}.

The optical activity is, however, very sensitive to some irregularities, e. g. disulfide linkages in polythiiranes, which by their chromophoric group can completely perturb the rotatory power. In such a case it is necessary to examine the ORD curves and better identify by CD all the chromophores present.

One must be also very careful in the case of l. m. w. polymers in which the end groups can strongly perturb the optical activity¹⁰. The effect of molecular weight on optical rotation dispersion was described in the case of PHB, together with a solvent dependence⁷¹. A dramatic solvent effect on

optical rotatory dispersion was observed in the case of poly(propylene oxide), which showed rotatory powers of opposite sign in benzene and chloroform solutions⁷². This effect was attributed to a change of polarisability of the methyl or methylene groups in benzene solution⁷². Oligomers of R-propylene oxide show variation in ORD depending on terminal groups and the solvent used⁷.

CONCLUSION

Considering the data reported above there are only few cases for which the properties of optically active and optically inactive materials were compared and usually only one particular property was studied in detail.

Nevertheless, the following general trends can be foreseen.

In polymers derived from monosubstituted monomers two kinds of behaviour were found: if the substituent is not very bulky, e.g. methyl, ethyl, the properties of polyenantiomers and their racemic mixture are very similar. On the other hand, if the substituent is a bulky group, e.g. *t*-butyl group, the melting behaviour, the crystalline structure, the solubility and some other properties can be very different for the polyenantiomer and the racemic isotactic polymer. The corresponding statistical polymer is usually amorphous.

In polymers having disubstituted asymmetric carbons the particular melting behaviour of the statistical stereocopolymer must be underlined.

It cannot be ascertained that there are marked differences in mechanical properties for all stereoisomeric polymers described above. However, it was demonstrated in some cases, e.g. polylactides, that some biological properties can be very strongly dependent on the enantiomeric composition. The same situation may occur in other applications, for example in pharmacologically active polymer drugs or drug polymeric carriers. The problem of block copolymers, polymers with reactive end or side groups, the combination of specific hydrophilic-hydrophobic properties in relation to the macromolecular chain structure, were not considered in this paper, but are of great interest, especially for biomedical applications.

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SAŽETAK**Utjecaj stereokemijske strukture na fizičko-kemijska svojstva polimera pripremljenih polimerizacijom otvaranja prstena kiralnih heterocikličkih monomera**

Nicolas Spassky, Alain Leborgne i Maurice Sepulchre

Uspoređena su fizičko-kemijska svojstva polimera pripremljenih polimerizacijom otvaranja prstena heterocikličkih kiralnih monomera s različitim enantiomernim sastavom. Opažena su dva osnovna tipa ponašanja produkata s monosupstituiranim asimetričnim ugljikom u lancu: kada supstituirana skupina nema veliku masu, svojstva polienantiomera i njihova racemička smjesa vrlo su slična: kada je masa supstituenta velika (npr. *t*-butil), mnoga svojstva istih polimera (talište, kristalna struktura, topljivost, itd.) vrlo su različita. Odgovarajući statistički stereokopolimeri jesu amorfni. Statistički stereokopolimeri polimera s disupstituiranim asimetričnim ugljikovim atomima su kristalni su, a njihovo taljenje mijenja se s enantiomernom čistoćom. U nekim je slučajevima opažena jaka ovisnost mehaničkih i bioloških svojstava stereokopolimera o enantiomernoj čistoći.