



UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL ATOMIC ENERGY AGENCY
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE: CENTRATOM TRIESTE



H4.SMR/916 - 22

SEVENTH COLLEGE ON BIOPHYSICS:
*Structure and Function of Biopolymers: Experimental and Theoretical
Techniques.*
4 - 29 March 1996

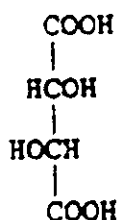
*Role of Chiral Conformations in the Development of Synthetic
Polymers*
and
*The Distinction between Biological Macromolecules and Chiral
Macromolecules which cannot distinguish Handedness*

Mark GREEN
Polytechnic University
New York
U.S.A.

"Towards the two tartaric acids, quinine does not behave like potash, simply because it is dissymmetric and potash is not."

----Louis Pasteur, 1860

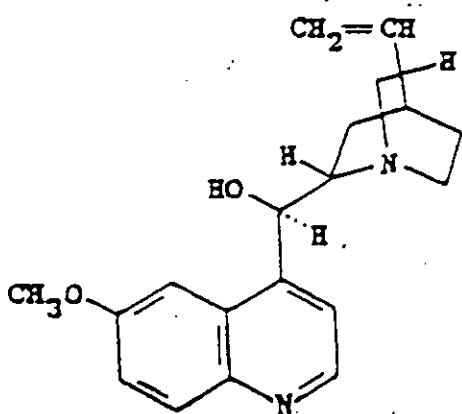
9039. L-Tartaric Acid.



9037. D-Tartaric Acid.



8075. Quinine.



"potash."

Also called "pearl ash,"

potassium carbonate.

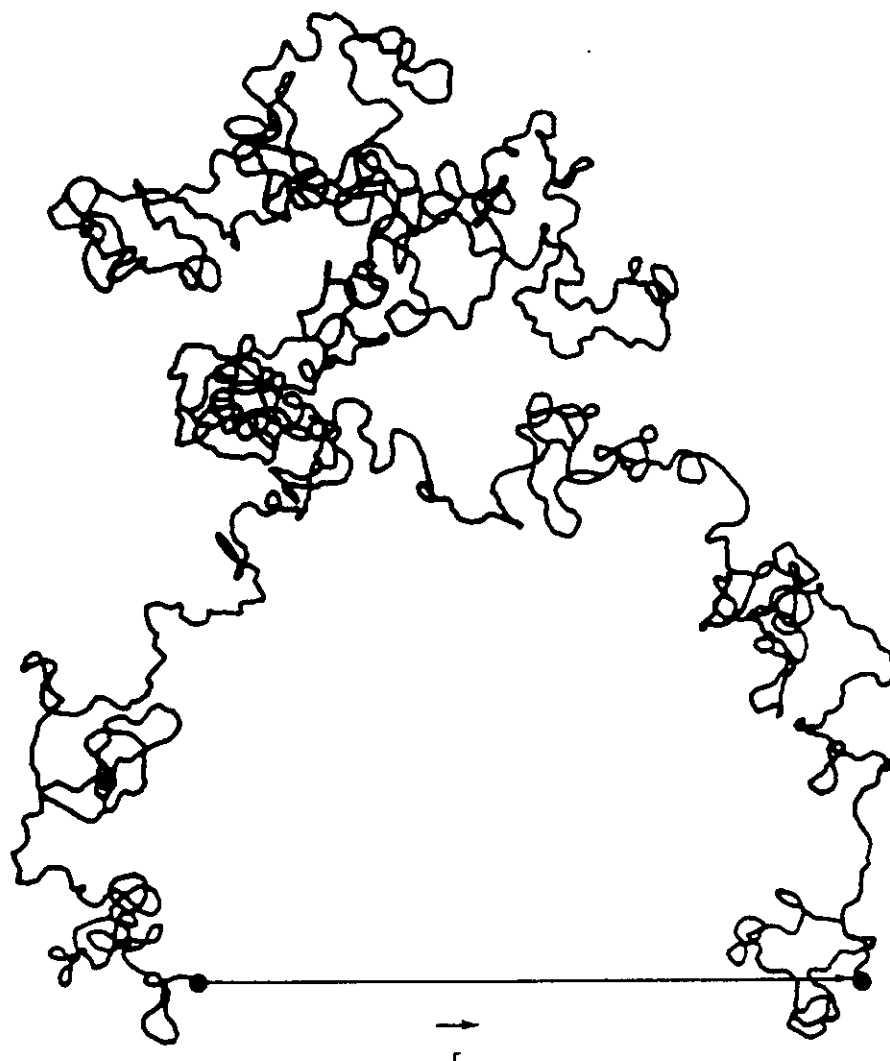


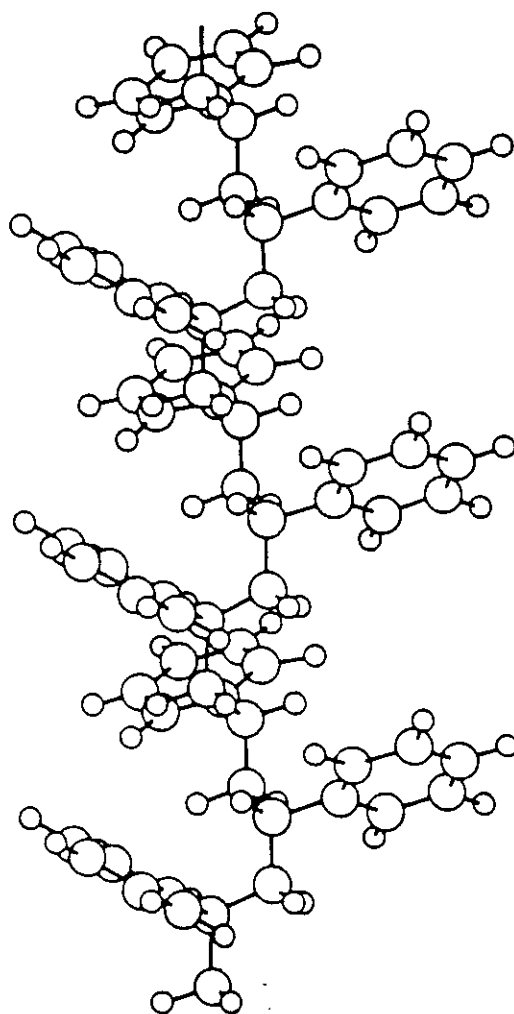
Figure 3.9. One conformation of a 1000 link polyethylene chain. Adapted from L. R. G. Treloar, *The Physics of Rubber Elasticity*, The Clarendon Press, Oxford. Reproduced by permission.

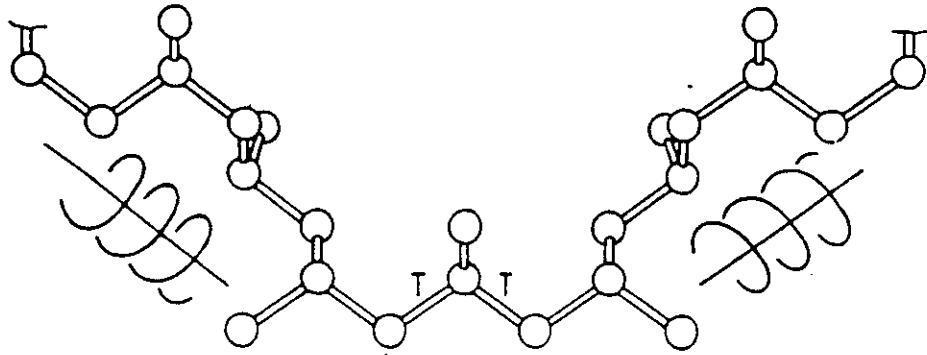
Leo Mandelkern

An Introduction to Macromolecules

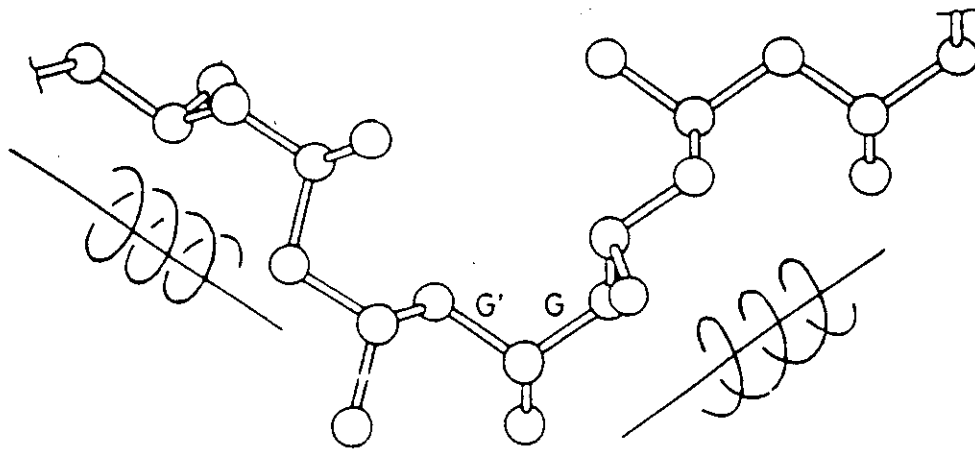
Second Edition

Fig. 7.9. Side view of the 3_1 helix of isotactic polystyrene (from Natta *et al.*, 1960).





(a)



(b)

Figure 15. Models of helix inversion in isotactic polypropylene: (a) TT conformation; (b) G'G conformation. From ref. (178); Copyright Accad. Naz. Lincei.

Table 1. Physical properties of poly-(S)-3-methyl-1-pentene fractions having different stereoregularity

Fraction	%	Sample A ¹⁾ Catalyst: Al(<i>i</i> -C ₄ H ₉) ₃ /TiCl ₄				
		[M] _B ²⁾ a) b)	[η] b)	m.p. (°C.)	$\frac{\Delta[M]_D}{\Delta T}$ a)	
Acetone sol.	6.3	+29.4	d)	n.d.	-0.08	
Acetone insol. diethyl ether sol. ...	2.6	+96.4	0.08	65-75 ^{e)}	-0.23	
Diethyl ether insol. isoctane sol. ...	0.9	+120	0.10	135-140 ^{e)}	-0.26	
Isoctane insol. benzene sol.	0.4	+158	0.11	175-180 ^{e)}	-0.34	
Benzene insol. decalin sol.	2.0	+161 ^{m)}	0.50	228-232 ^{e)}	-0.36	
Residue	87.8	n.d.	n.d.	271-273 ^{g)}	n.d.	

Optically Active Vinyl Polymers

IX. Optical Activity and Conformation in Dilute Solution of Isotactic Poly- α -Olefins

By P. PINO, F. GAMBELLI, G. P. LORENZI, and G. MONTAGNOLI

Dedicated to Prof. G. NATTA on the occasion of his 60th birthday

(Eingegangen am 4. Dezember 1962)

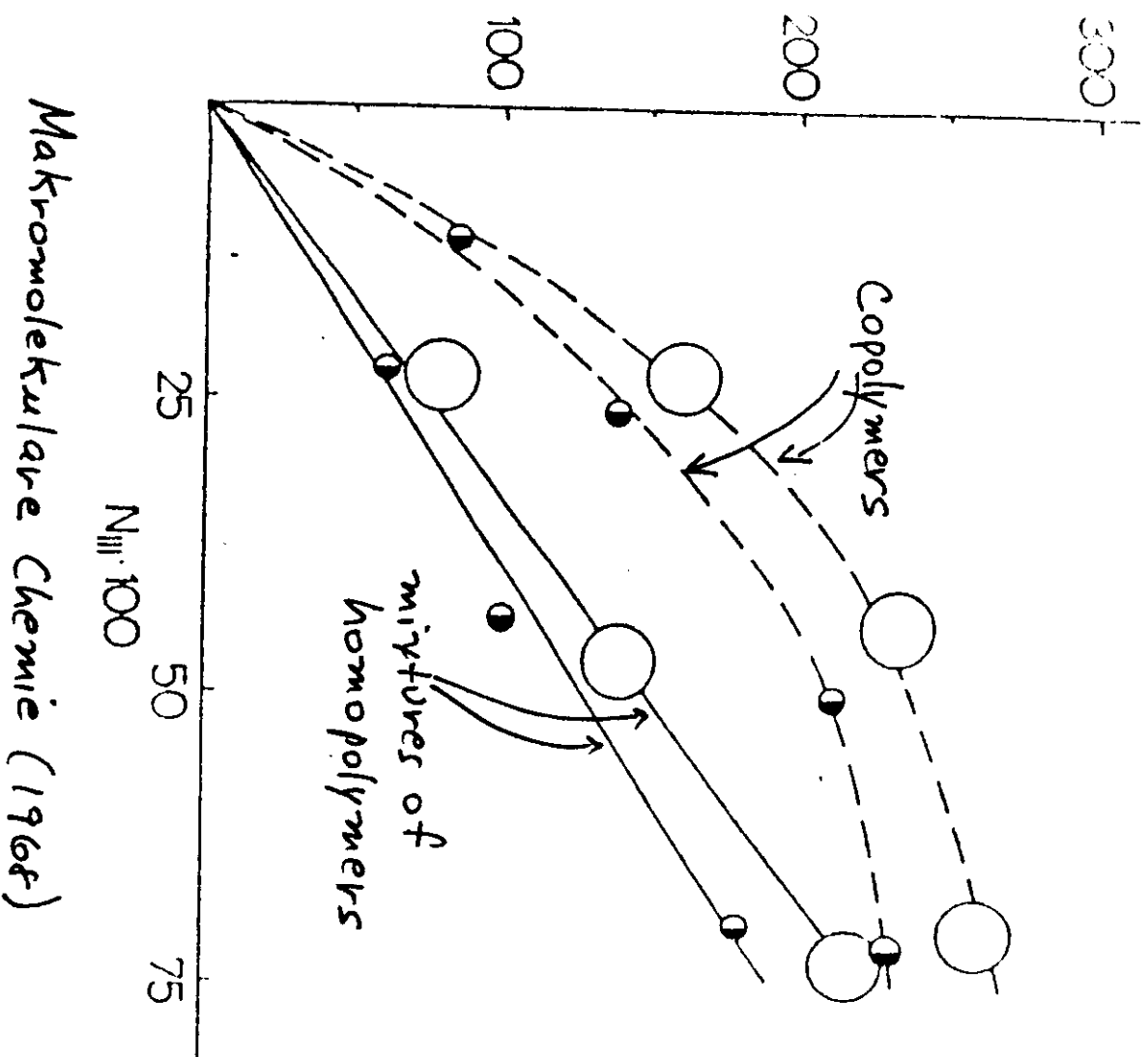
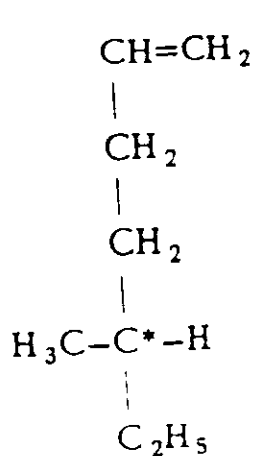


Fig. 1. Rotatory power in methylcyclohexane vs. mole fraction of units derived from (S)-4-methyl-1-hexene (N_{III}) for copolymers of (S)-4-methyl-1-hexene with 4-methyl-1-pentene (dashed line) and for mixtures of the two homopolymers (solid line) (● fraction extracted with ethyl acetate; ○ fraction extracted with cyclohexane)

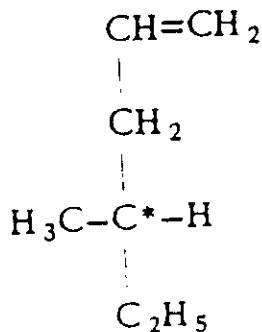
ON THE RELATIONSHIP BETWEEN MONOMER OPTICAL
 PURITY AND POLYMER ROTATORY POWER IN
 SOME LINEAR POLY- α -OLEFINES

Polymer Letters, 5, 307 (1967)

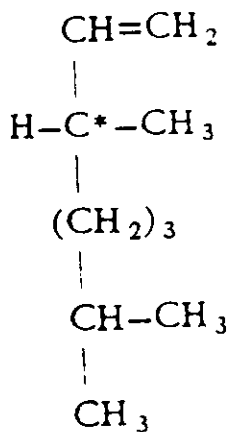
P. Pino, F. Ciardelli, G. Montagnoli, O. Pieroni



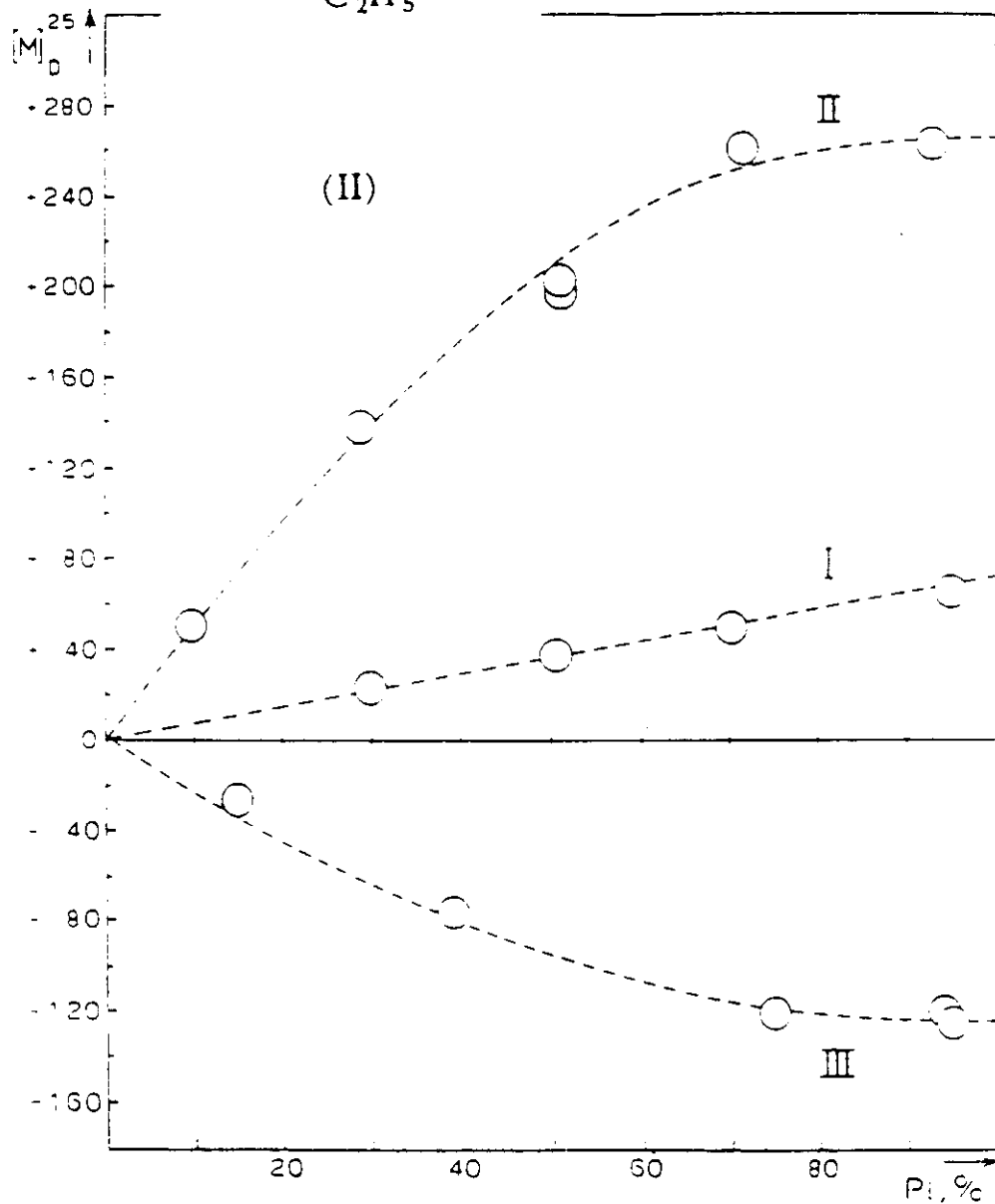
(I)



(II)



(III)



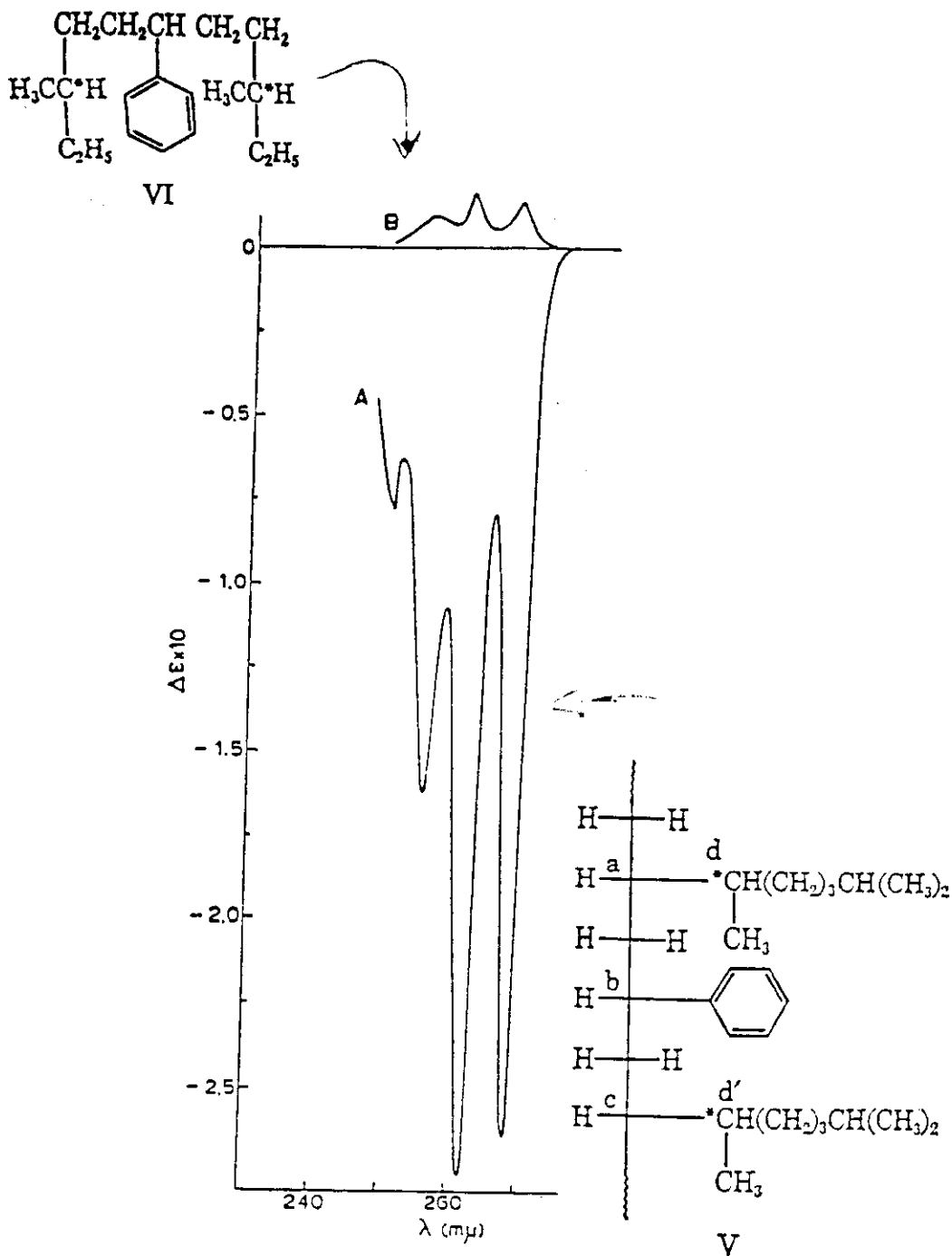
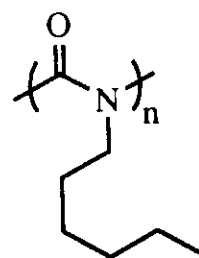
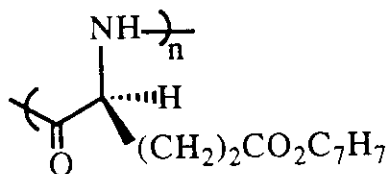
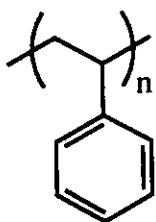


Figure 1. Circular dichroism in chloroform solution at 25° of (3*S*,9*S*)-3,9-dimethyl-6-phenylundecane (B) and of the diethyl ether extractable fraction (Table I) of the styrene-(*R*)-3,7-dimethyl-1-octene copolymer (A); $\Delta\epsilon$ is based on one unit of III deriving from styrene.¹²

Piero Pino, Carlo Carlini, Emo Chiellini
 Francesco Ciardelli, Piero Salvadori
Istituto di Chimica Organica Industriale dell'Università
Sezione IV del Centro Nazionale di Chimica
delle Macromolecole del C.N.R.
Pisa, Italy
 Received May 18, 1968

Dependence of Radius of Gyration (R_G)
on Degree of Polymerization (n)



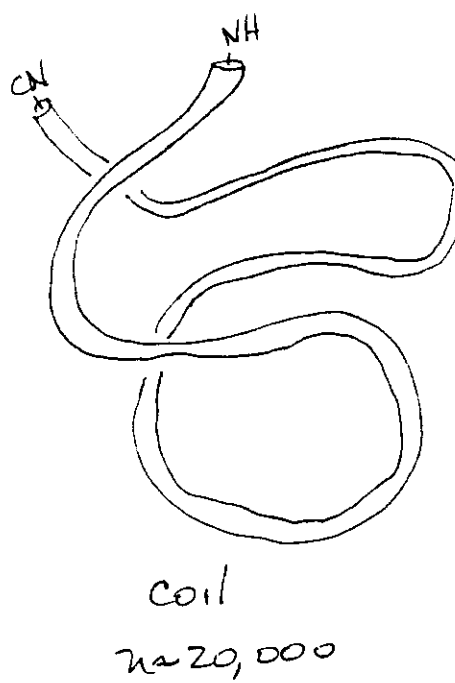
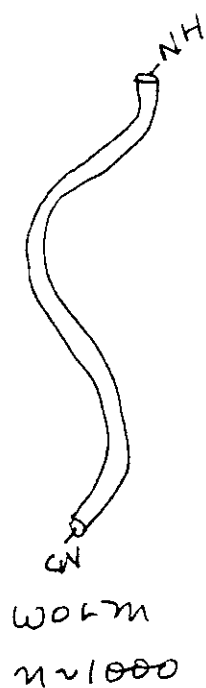
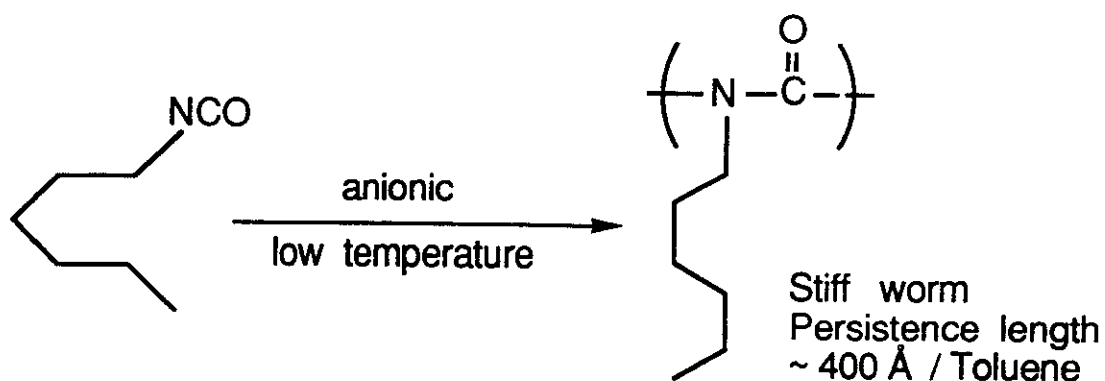
n	$R_G, \text{Å}$
2200	160
5000	220
17,000	440

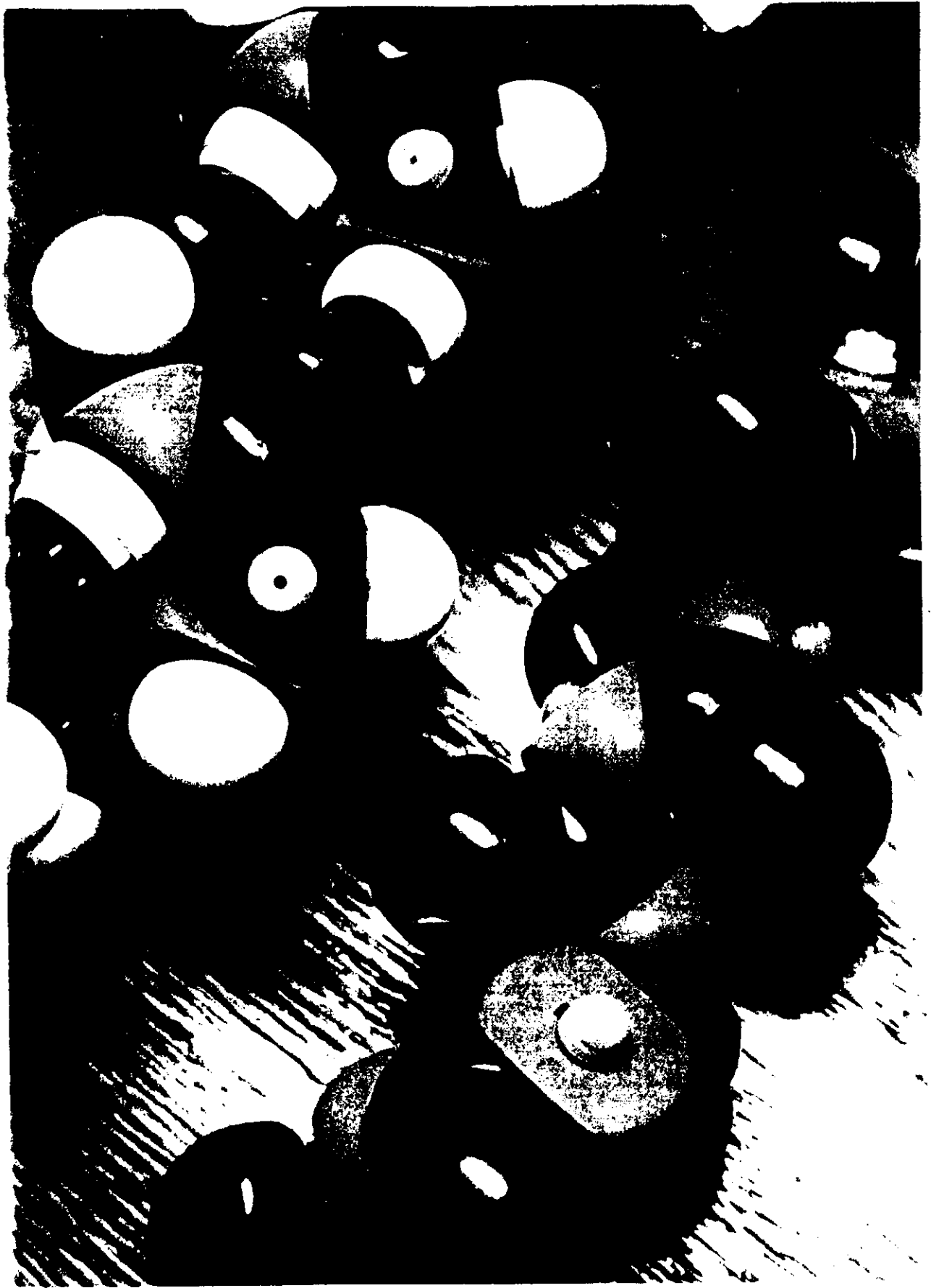
n	$R_G, \text{Å}$
700	260
1400	530
2700	890

n	$R_G, \text{Å}$
300	162
622	301
3300	970

Polyisocyanates ~ Nylon-1

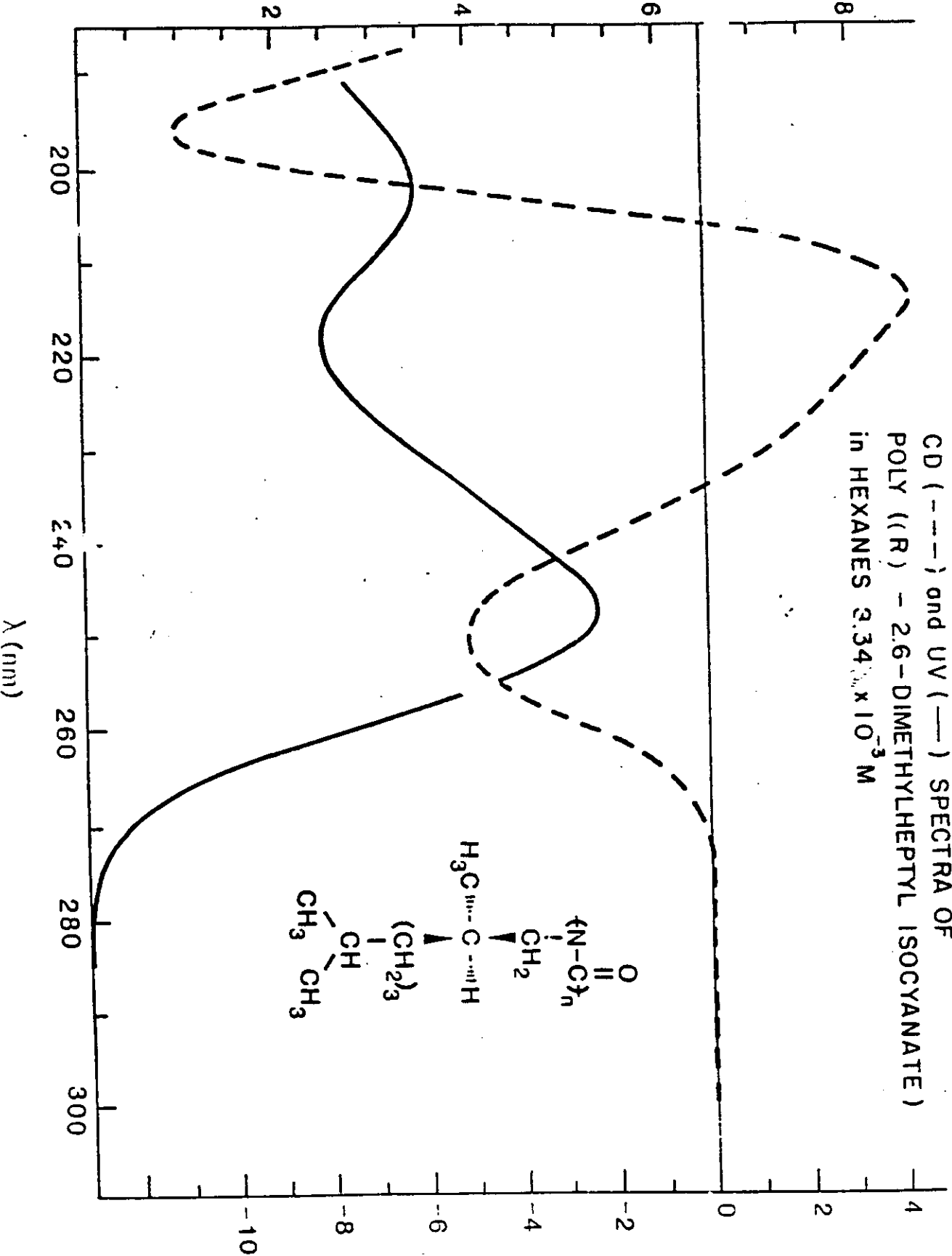
DuPont Creation ~ 1959



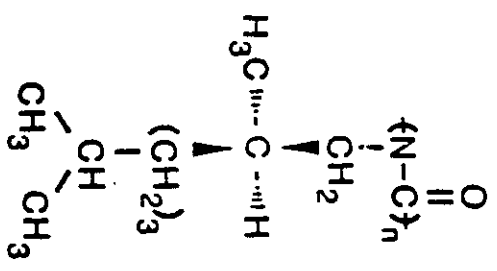




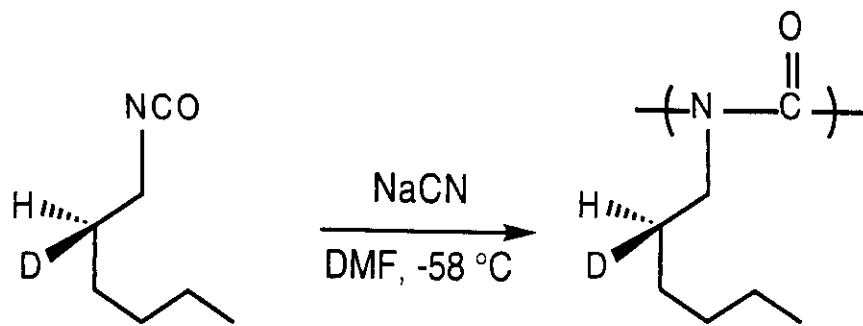
$\epsilon \times 10^{-3} \text{ L mole}^{-1} \text{ cm}^{-1}$



CD (---) and UV (—) SPECTRA OF
 POLY ((R) - 2,6-DIMETHYLHEPTYL ISOCYANATE)
 in HEXANES $3.34 \times 10^{-3} \text{ M}$

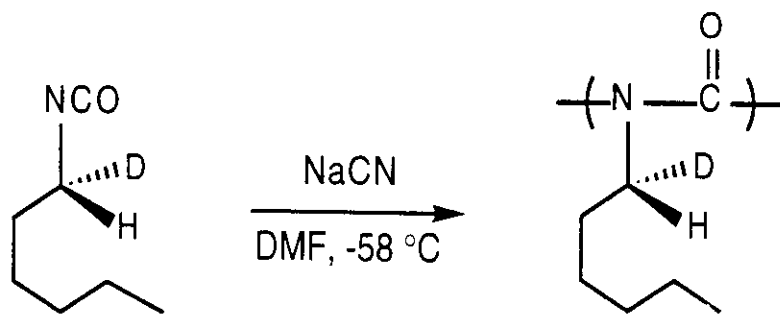
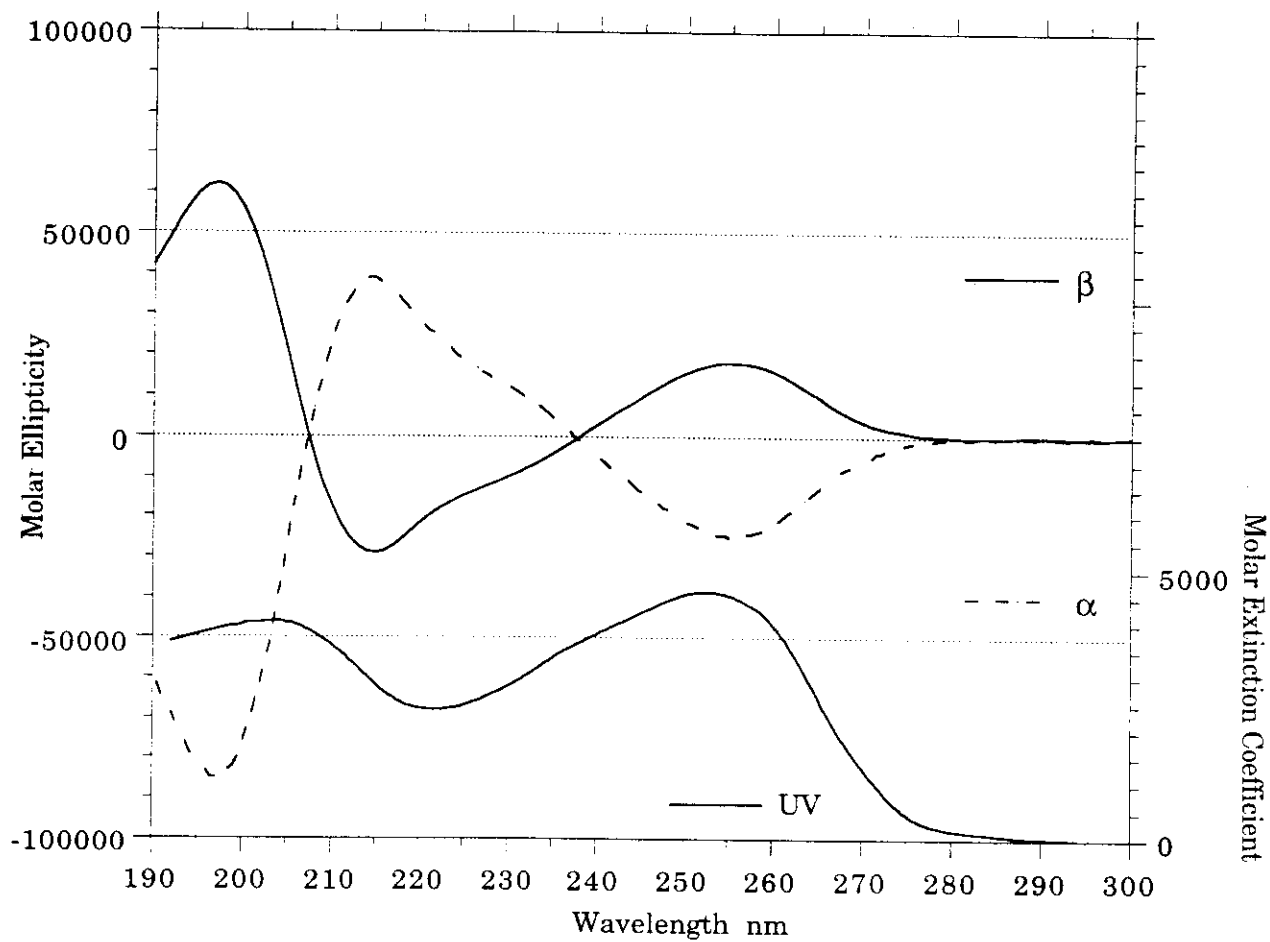


$[\theta] \times 10^{-4} \text{ deg cm}^2 \text{ dmole}^{-1}$



$[\alpha]_D = -0.43$ (neat)

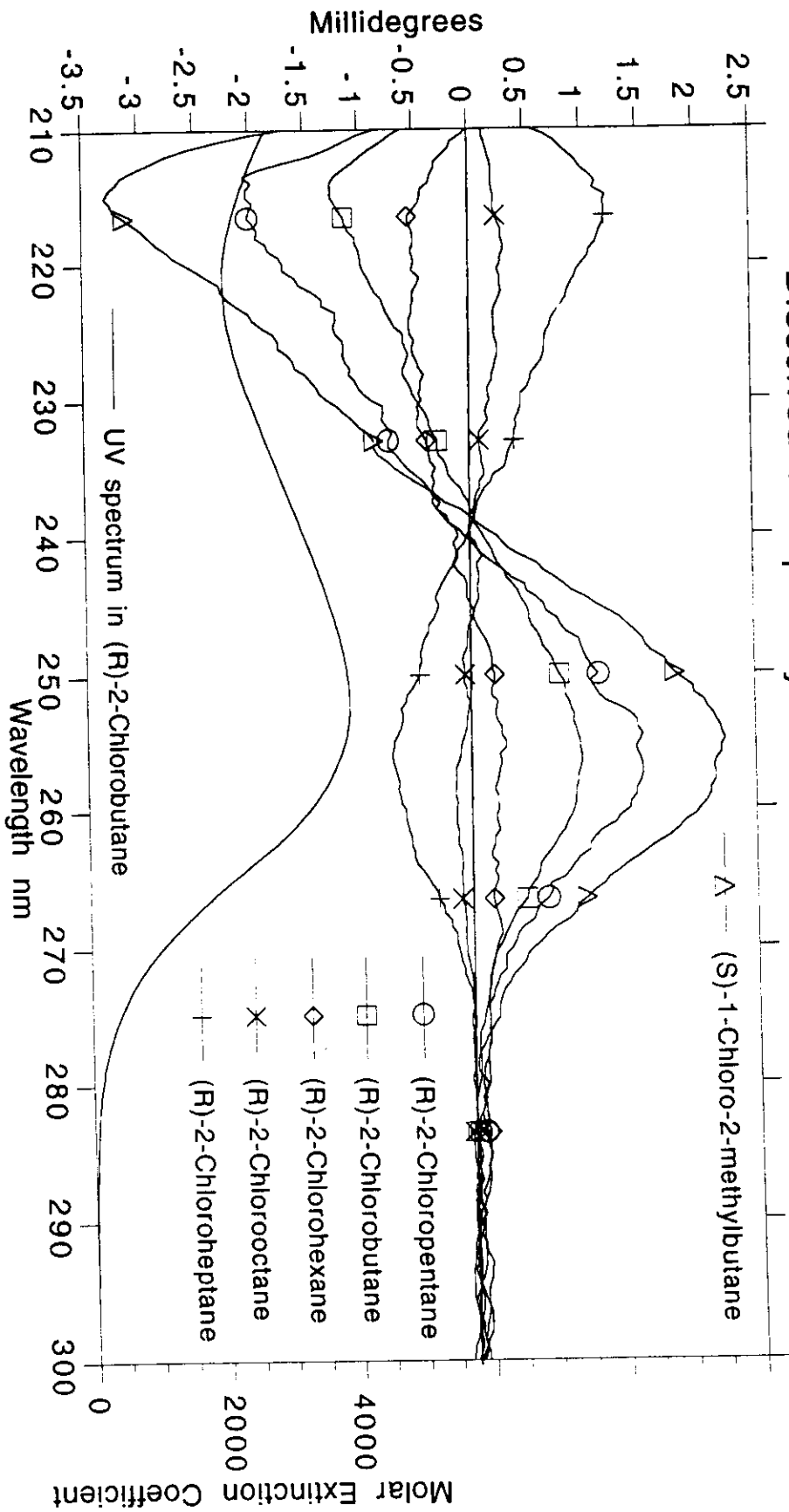
$[\alpha]_D = +302$ (n-hexane)



$[\alpha]_D = +0.65$ (neat)

$[\alpha]_D = -444$ (n-hexane)

Circular Dichroism Spectra of Poly(*n*-hexyl isocyanate) Dissolved in Optically Active Solvents at 20 °C^{a,b}



^a Ultra-violet spectrum (—) shown only for (R)-2-chlorobutane. Please see the text.
^b Continuous lines represent the experimental data; all concentrations of polymer are 1.9 mg/mL

Statistical Thermodynamic Expression for Cooperation in Optically Active Polyisocyanates

$$\frac{[\alpha]}{[\alpha]_m} = \frac{(\delta u / w) \cdot (1 - v / (w + v)) w N - \exp(-2 w N) [(w - v) / (w + v) - v / (w + v) w N]}{(1 + \exp(-2 w N) (w - v) / (w + v))}$$

Short chains

Long chains

$$\ln \frac{[\alpha]_m + [\alpha]}{[\alpha]_m - [\alpha]} = N (2 G_h) / RT$$

$$\frac{[\alpha]}{[\alpha]_m} = \frac{(e^{G_r/RT}) (G_h)}{RT} / \left((e^{G_r/RT} \frac{G_h}{RT})^2 + 1 \right)^{1/2}$$

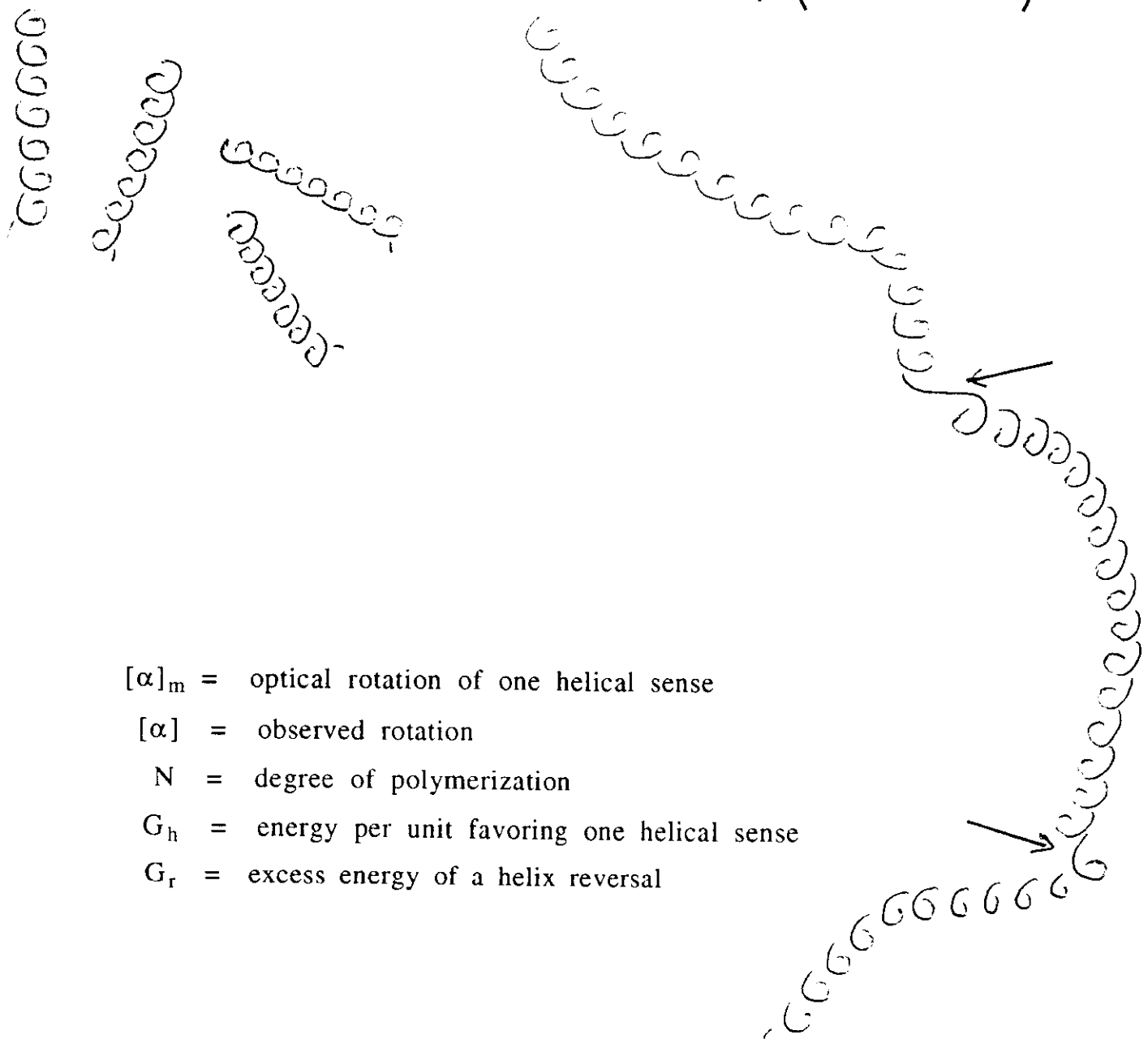
$[\alpha]_m$ = optical rotation of one helical sense

$[\alpha]$ = observed rotation

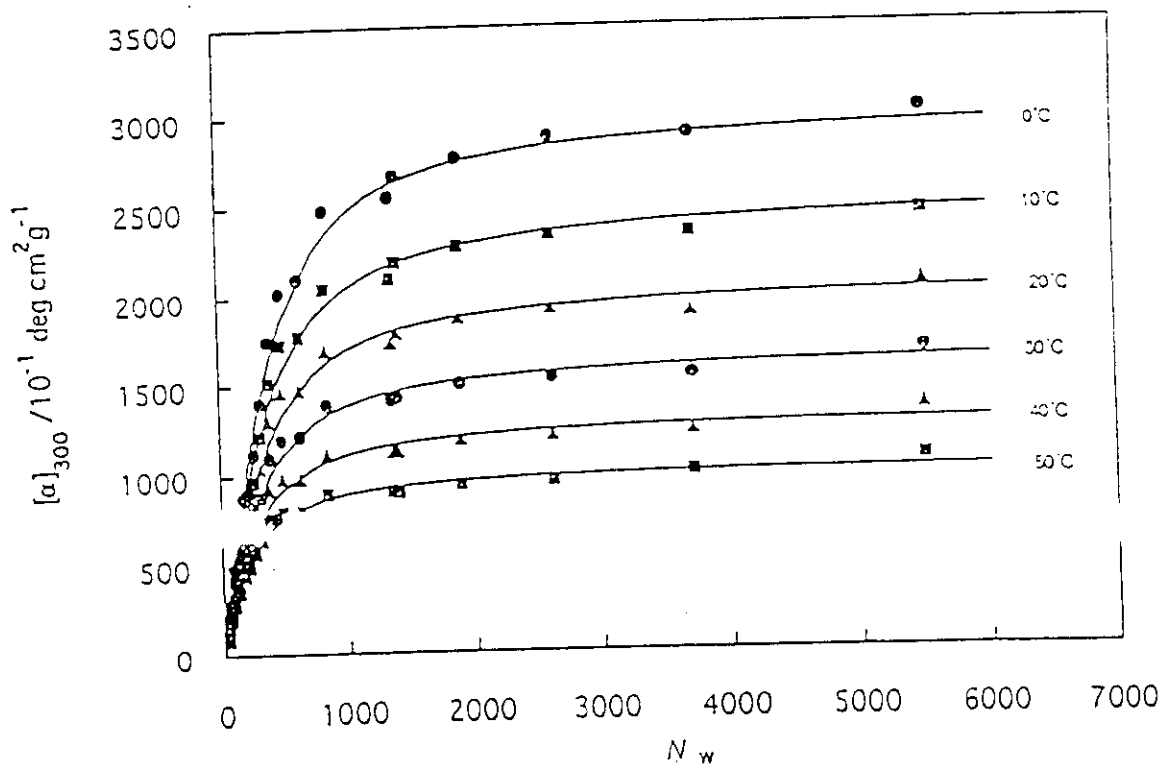
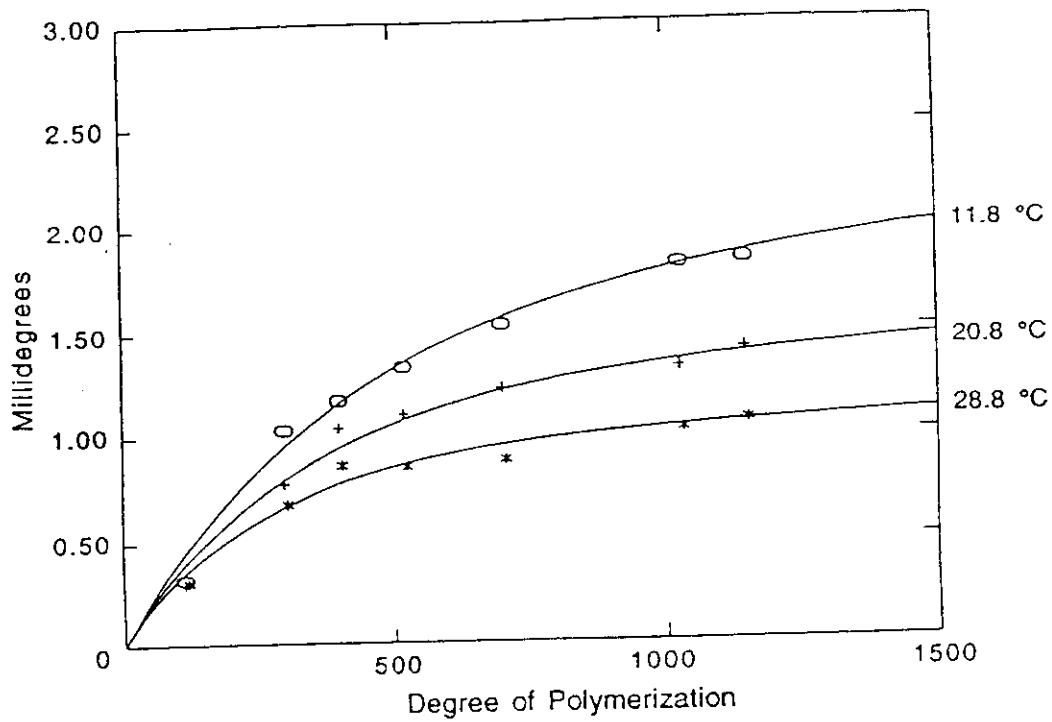
N = degree of polymerization

G_h = energy per unit favoring one helical sense

G_r = excess energy of a helix reversal



Experimental and Theoretical Dependence on Degree of Polymerization and Temperature of the Optical Activity for Poly(n-hexyl isocyanate) Dissolved in (R)-2-Chlorobutane^a



Dependence of $[\alpha]_{300}$ on degree of polymerization for fractionated β -PdHIC in 1-chlorobutane at indicated temperatures. Marks, experimental data; solid curves, theoretical values calculated

Thermodynamic parameters favoring one helical sense

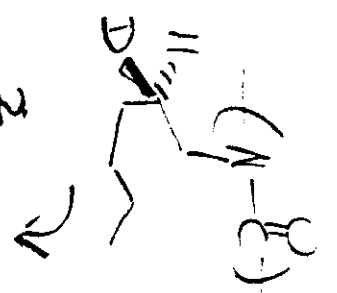
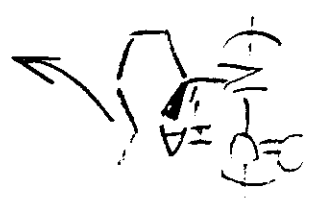
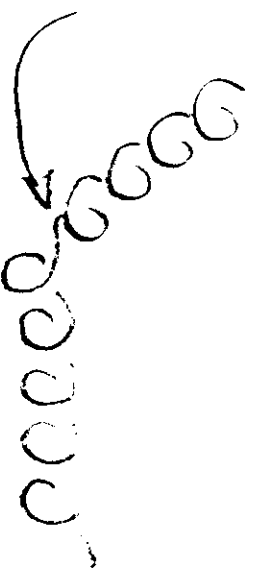


Table 3. Free Energy Parameters and Statistical Averages for Poly((R)-*P*-deuterio-*n*-hexyl isocyanate) and Poly((R)-1-deuterio-*n*-hexyl isocyanate) in Solution

	poly((R)-1-deuterio- <i>n</i> -hexyl isocyanate)				poly((R)-2-deuterio- <i>n</i> -hexyl isocyanate)			
	hexane	1-chlorobutane	dichloromethane	hexane	1-chlorobutane	dichloromethane		
$2AH_n$ /(cal mol ⁻¹)	-3.25	-6.01	-10.4	1.94	2.82	3.22		
$2AS_n$ /(cal K ⁻¹ mol ⁻¹)	-0.0062	-0.014	-0.027	0.0040	0.0063	0.0080		
T_M/K	530	440	390	480	450	400		
$2AG_f$ /(cal mol ⁻¹)	-1.40	-2.0	-2.60	0.76	0.97	0.91		
ΔG_f /(cal mol ⁻¹)	3890	3640	3250	3870	3530	3210		
$\mu M/\mu P$	1.0025	1.00340	1.00450	0.99870	0.99830	0.99840		
ν	0.0015	0.00190	0.0038	0.0013	0.0024	0.0040		
n_M/n_P	3.7	4.1	2.9	0.45	0.54	0.70		
$ \alpha / \alpha _M$	-0.573	-0.610	-0.488	0.375	0.315	0.196		
n_v	2.40	3.1	6.6	2.4	4.5	8.0		

20 °C, N = 2000

Excess Free Energy of Helical Reversal



Hydration forces between phospholipid bilayers

R.P. Rand¹ and V.A. Parsegian²

¹Department of Biological Sciences, Brock University, St Catharines, Ontario (Canada) and ²DCRT/NIDDK, National Institutes of Health, Bethesda, MD (U.S.A.)

that they come from virtually undetectable perturbations of solvent summed over large numbers of water molecules.

these simulations are accurate to some 0.5 kcal/mol of solvent (e.g., Ref. 106) while the perturbations of water that seem to be important are as small as approx. 1 cal/mol

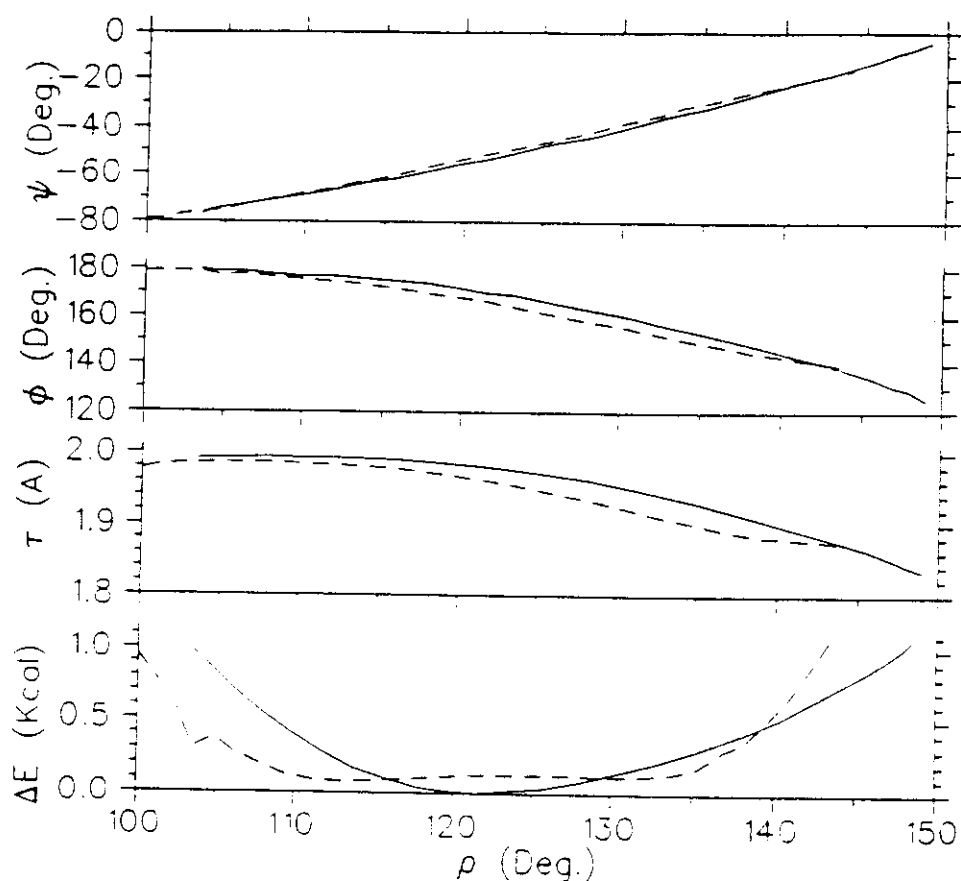
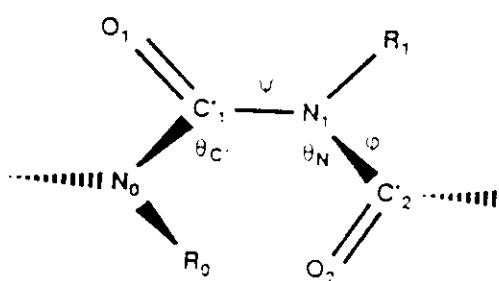


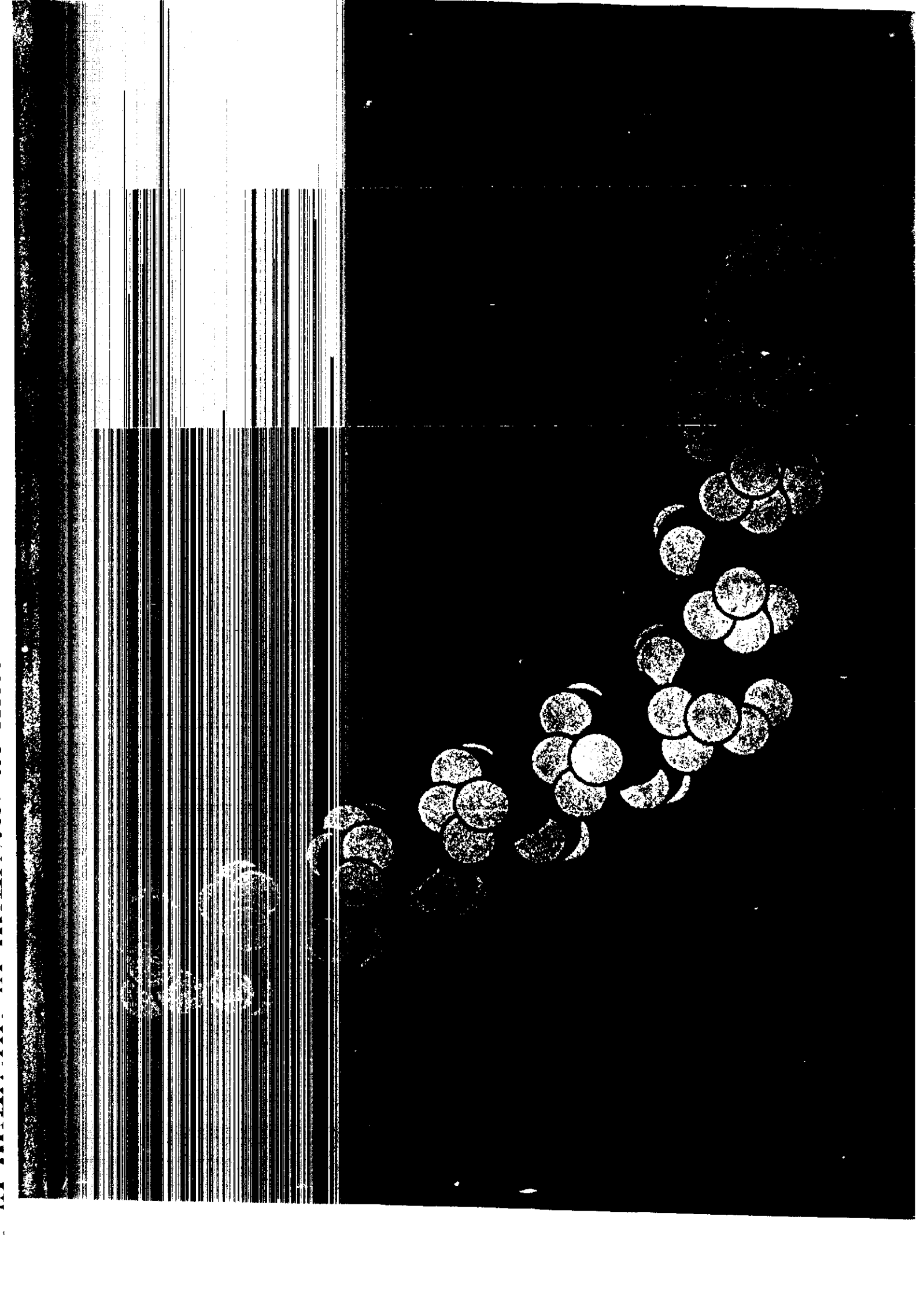
Figure 5. Excess energy ΔE , helical displacement τ , and backbone torsional angles ϕ and ψ , all as functions of the helical rotation ρ in PBIC, for conformations 1 (continuous lines) and 2 (dashed lines)..

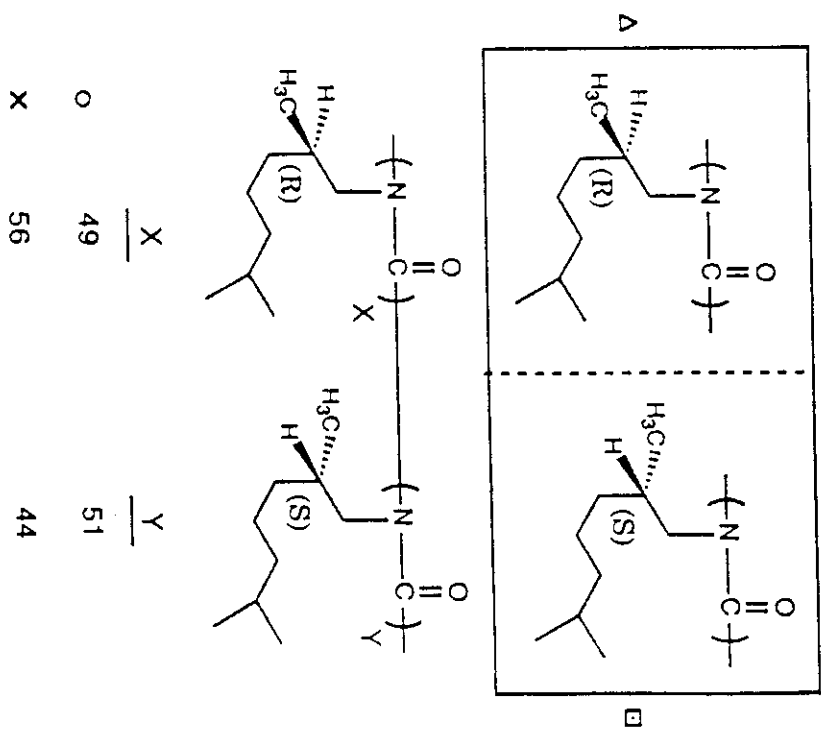
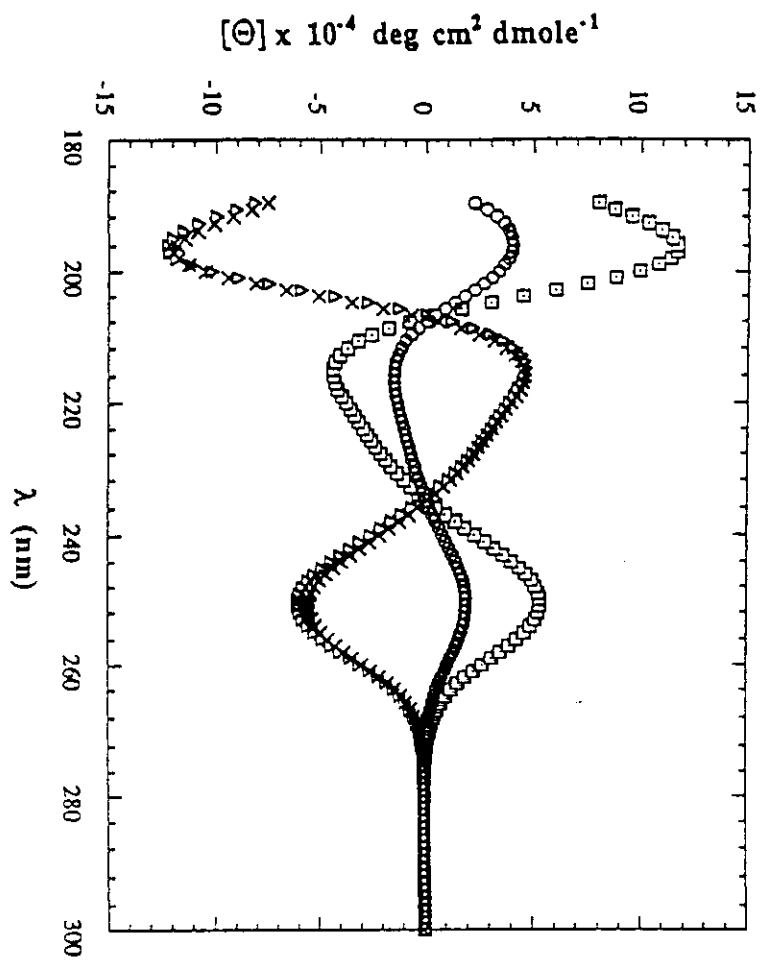
τ = monomer projection length



ρ = rotation/monomer

Soft collective motion allows a range of helical states which differ in conjugation and therefore in their UV absorption maxima





Theory of Chiral Order in Random Copolymers

Jonathan V. Selinger Center for Bio/Molecular Science and Engineering, Naval Research Laboratory

Robin L. B. Selinger Materials Science and Engineering Laboratory, National Institute of Standards and Technology

Theoretical argument: The random copolymer maps onto the random-field Ising model.

Hamiltonian:
$$H = -J \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} - \sum_{i=1}^N h_i \sigma_i$$

Random field:
$$h_i = +h \text{ with probability } p$$

$$h_i = -h \text{ with probability } 1 - p$$

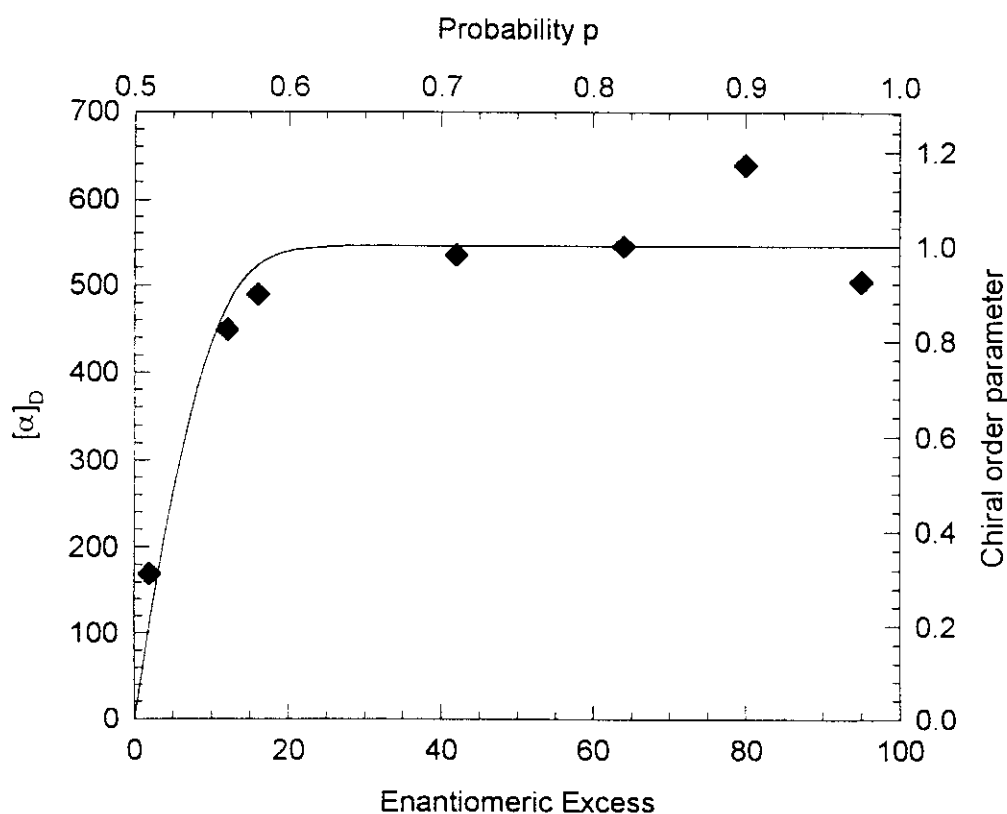
Random copolymer:	Random-field Ising model:
Local direction of helix	Ising spin σ_i
Chirality of monomer	Random field h_i
Enantiomeric excess Δ	Probability $p = (1 + \Delta)/2$
Energy cost of helix reversal	Ising exchange constant $2J=4$ kcal/mol
Energy cost of right-handed monomer in left-handed helix (or vice versa)	Magnitude of random field $2h=0.4$ kcal/mol
Chiral order parameter (measured by optical activity)	Magnetization $M = \frac{1}{N} \sum_{i=1}^N \sigma_i$

An approximate calculation gives $M = \text{erf}\left(\sqrt{2L}\left(p - \frac{1}{2}\right)\right)$,

where L is the size of a domain of constant helicity.

The Imry-Ma argument for the random-field Ising model gives $L \approx (J/h)^2 = 100$. Numerical calculations, extrapolated to limit of long chains, give $L \approx 164$.

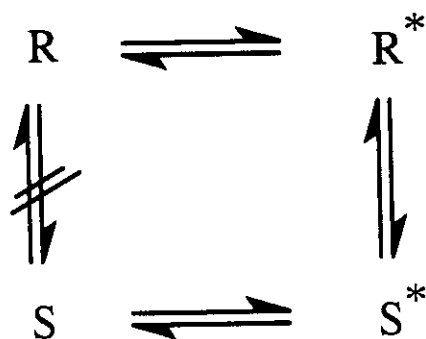
Comparison with experiment:



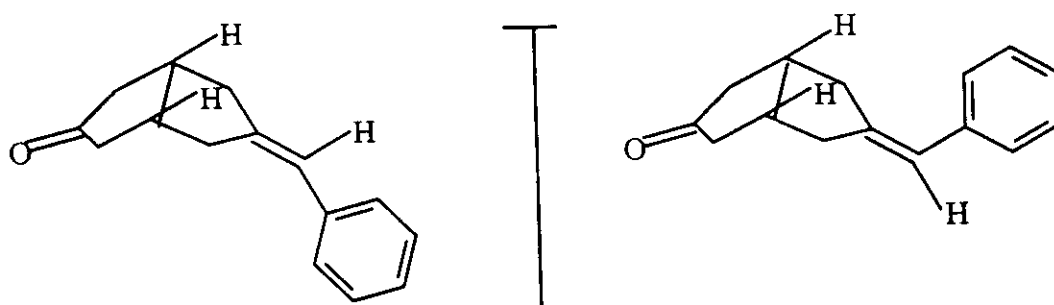
Good agreement with theoretical prediction, with *no adjustable parameters* (other than the overall scale factor between $[\alpha]_D$ and the chiral order parameter M).

Y. Inoue, Chemical reviews, 1992, 92(5), 741: Asymmetric Photochemistry

"..... the photoderacemization of organic compounds, in the strict sense, has scarcely been explored."

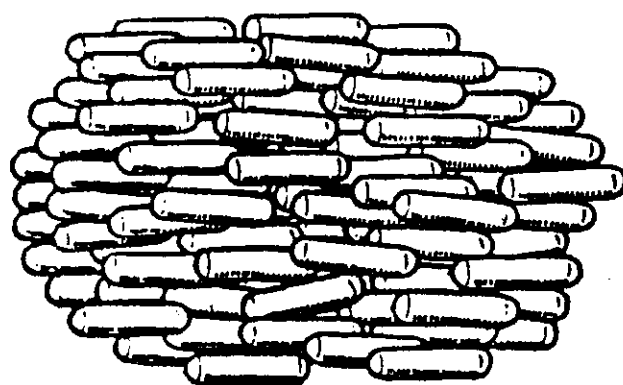
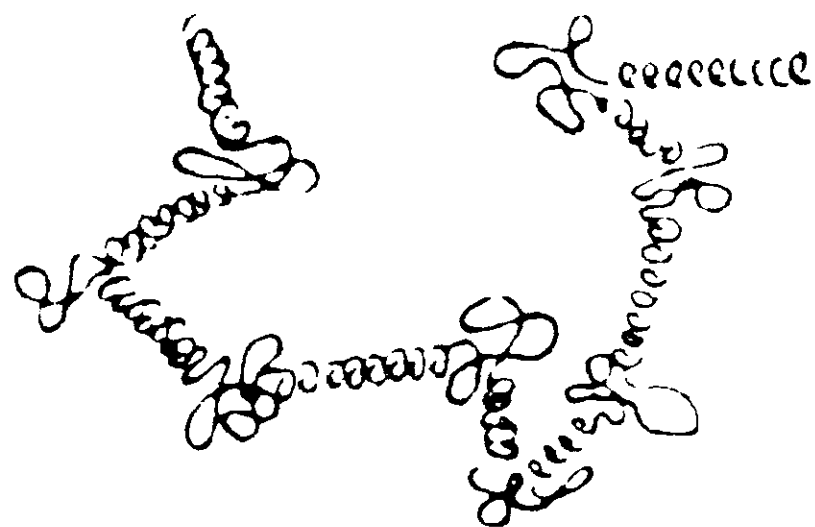


G.B.Schuster, Georgia Tech.



A.R.Khokhlov and A.N.Semenov, Moscow, USSR
Macromolecules, 1984.

"Liquid crystalline phase -----flexibility
constitutes the next problem".



nematic

A.M.Gupta and S.F.Edwards, Cambridge, England
Journal of Chemical Physics, 1993.

"----- the conformations of a chain in dilute
solution can be different from that in the nematic
state. To our knowledge this assumption has not
been tested".

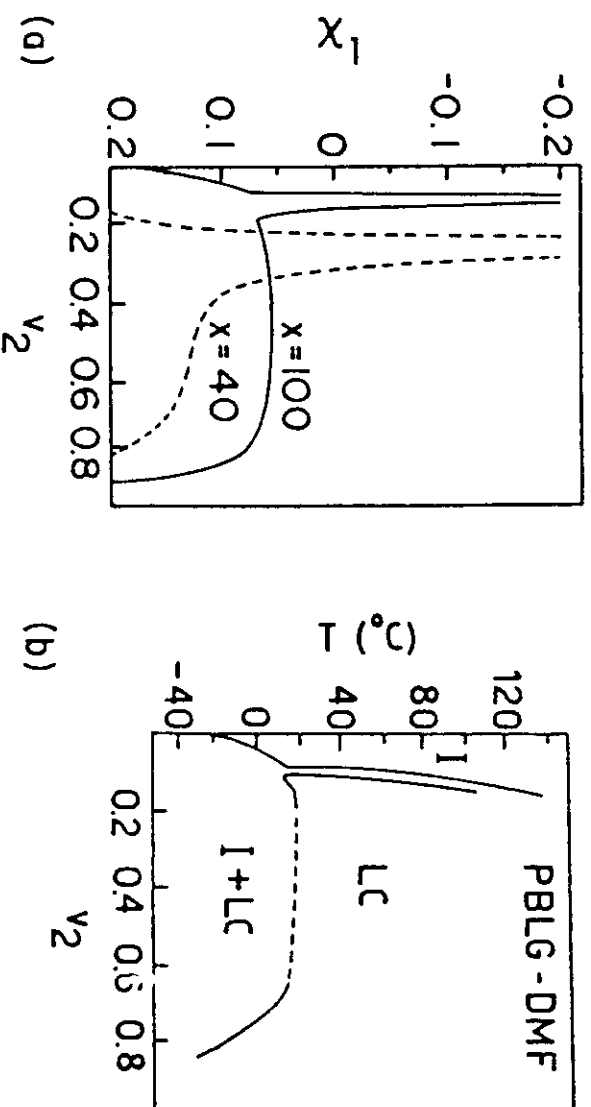
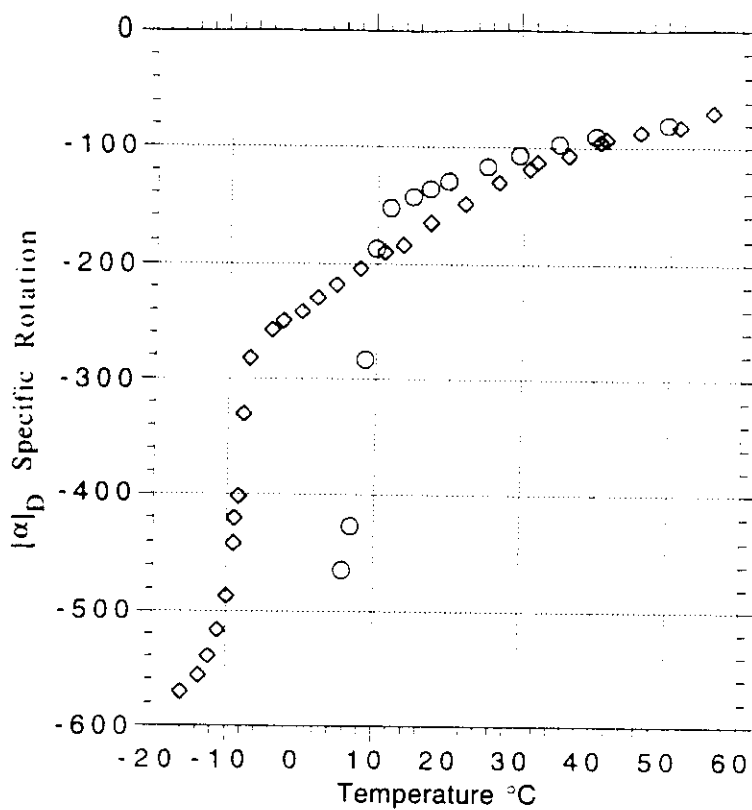


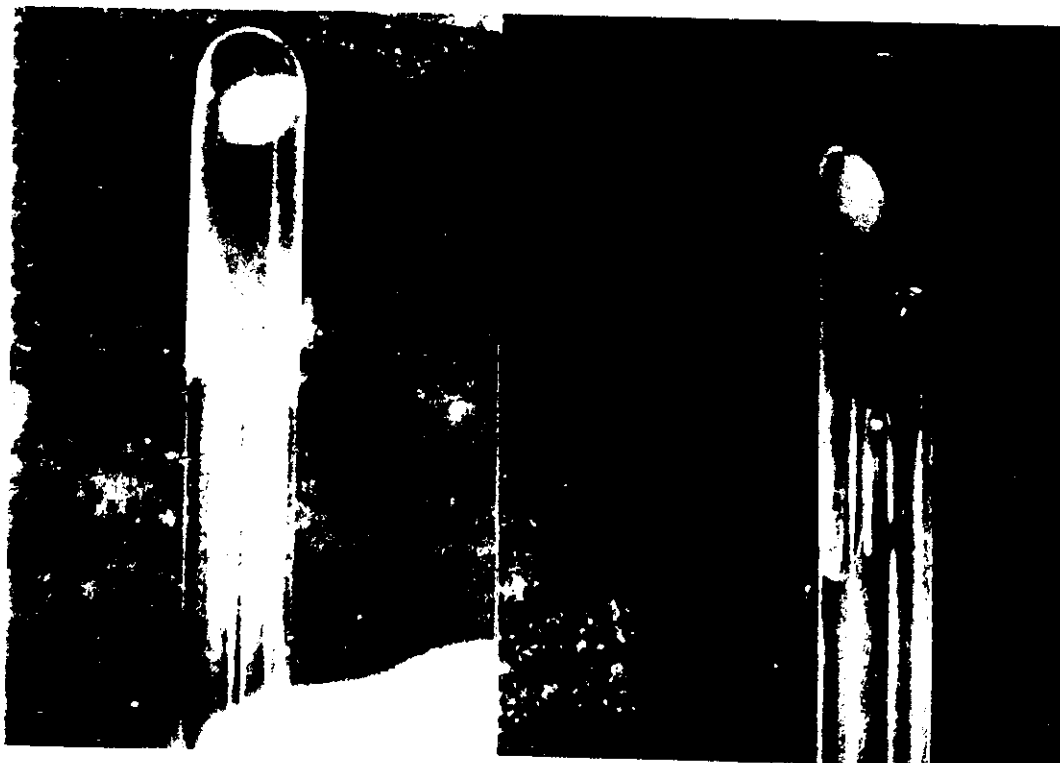
Fig. 5. (a) Theoretical phase diagrams for rigid rods according to Flory (1956a) for axial ratios of 100 and 40. (b) Experimental phase diagrams for PBLG in DMF reported by Miller *et al.* (1974).

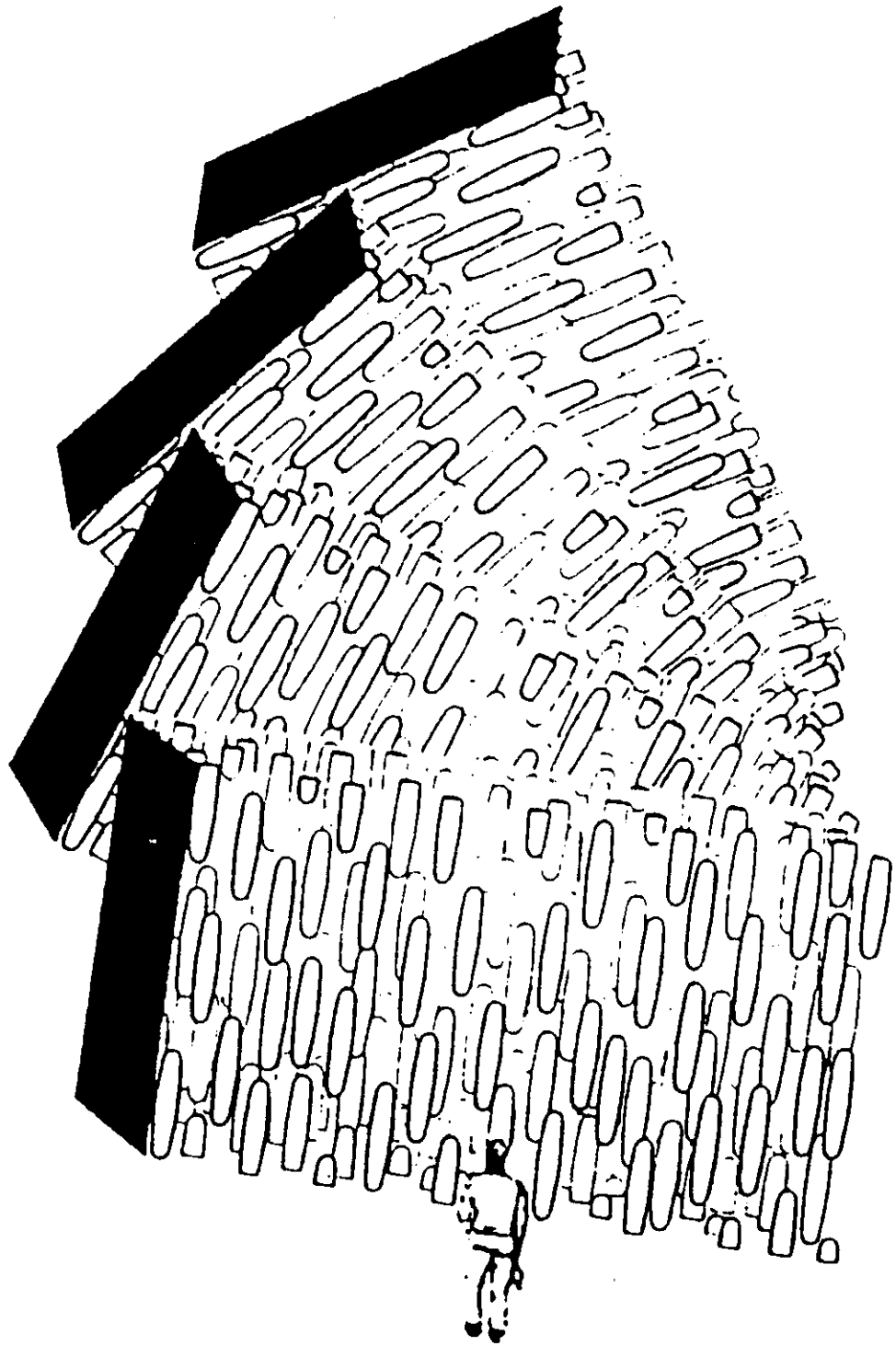


○ $[\alpha]_D$ in n-octane (1.5×10^{-4} g/ml)

◇ $[\alpha]_D$ in n-hexane (4.24×10^{-4} g/ml)

Optical rotation versus temperature for a copolymer of 99.5 % n-hexyl isocyanate and 0.5 % (R)-2,6-dimethylheptyl isocyanate





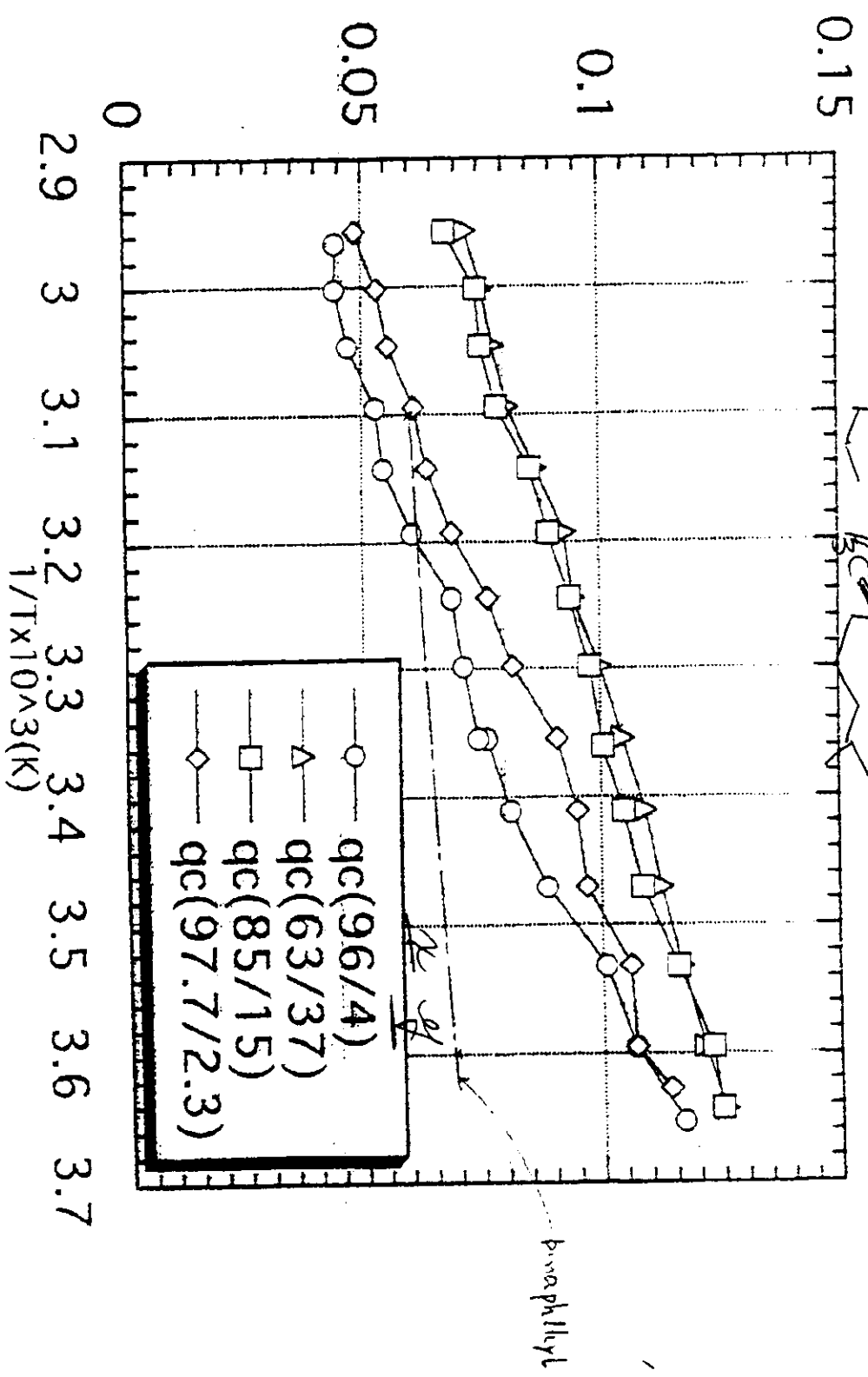
Lyotropic Nematic Phase doped with chiral

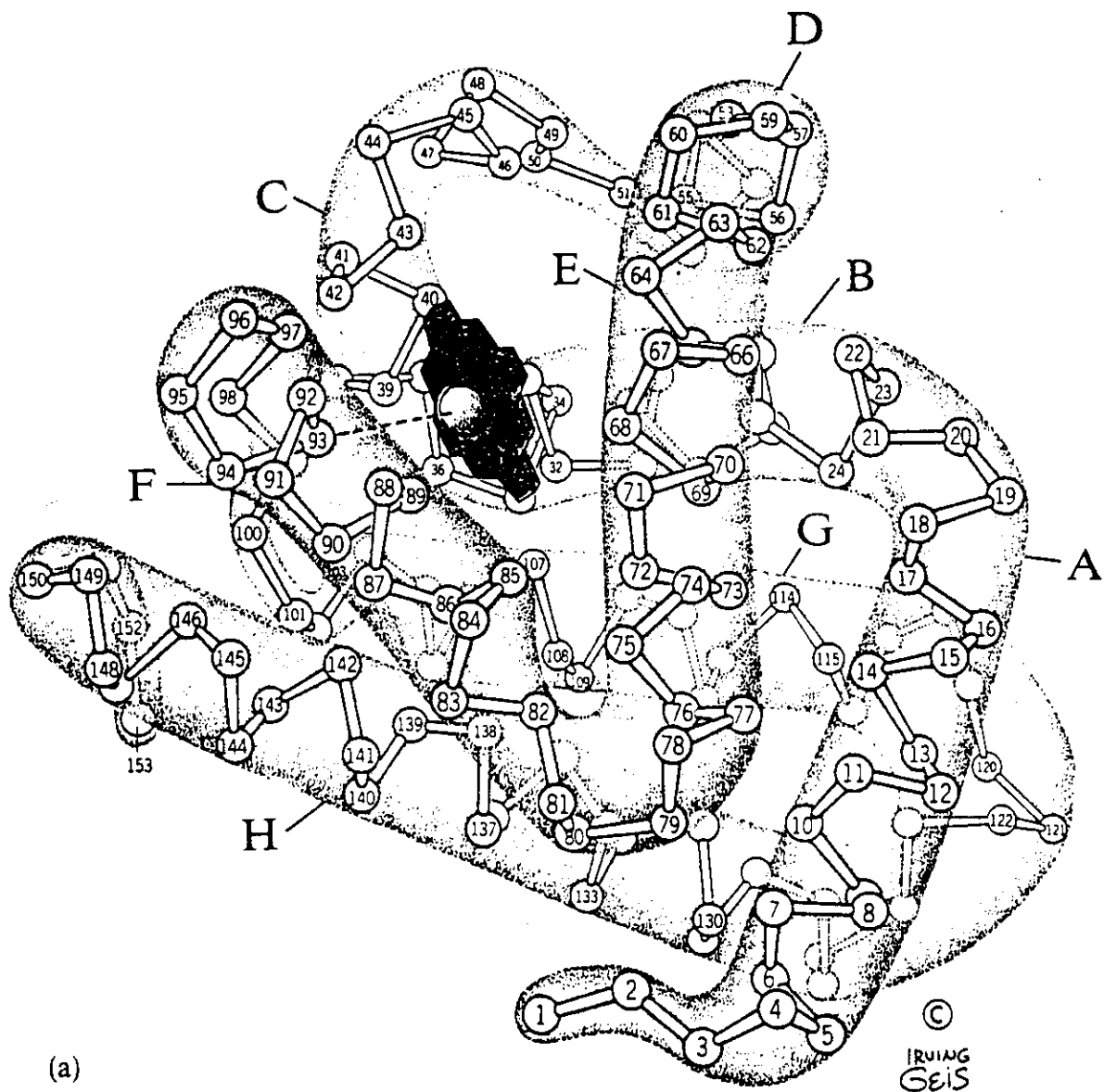
Copolymers:



Forms Cholesteric phase

$$\frac{2\pi}{\text{pitch}} = \delta$$





(a)

Figure 1-4

Three typical protein tertiary structures. (Only α -carbon positions are shown.) (a) Myoglobin consists mostly of α helices, labeled A through H, and contains a heme group (colored) that binds oxygen. [Drawing by Irving Geis.]

Cholesteric Theory

$$q_c = \frac{2\pi}{\text{pitch}} \quad ; \quad G = G_0 + (\delta G / \delta q_c) q_c + 1/2 (\delta^2 G / \delta q_c^2) q_c^2$$

where: $\delta^2 G / \delta q_c^2 = K_{22}$

For Polymer Lyotropic Liquid Crystals:

$$K_{22} = -T (\delta^2 S / \delta q_c^2)$$

therefore at equilibrium:

$$q_c = \frac{\delta H / \delta q_c}{T (\delta^2 S / \delta q_c^2)} - \frac{\delta S / \delta q_c}{\delta^2 S / \delta q_c^2}$$

J. P. STRALEY

14

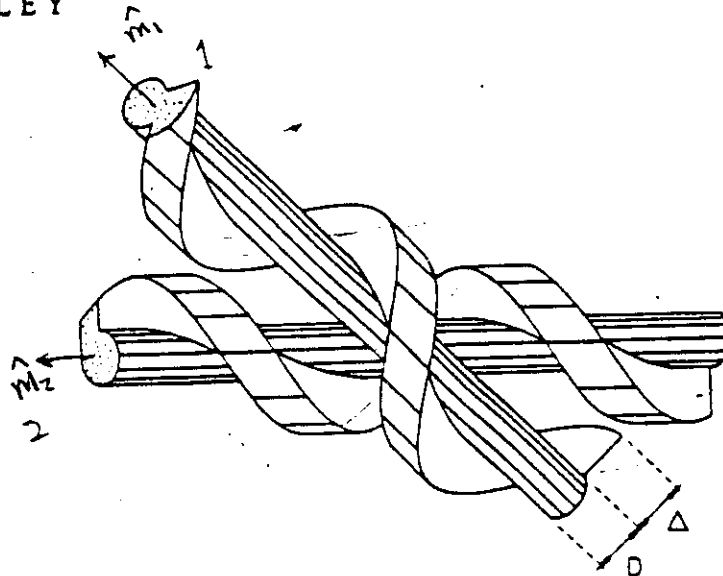
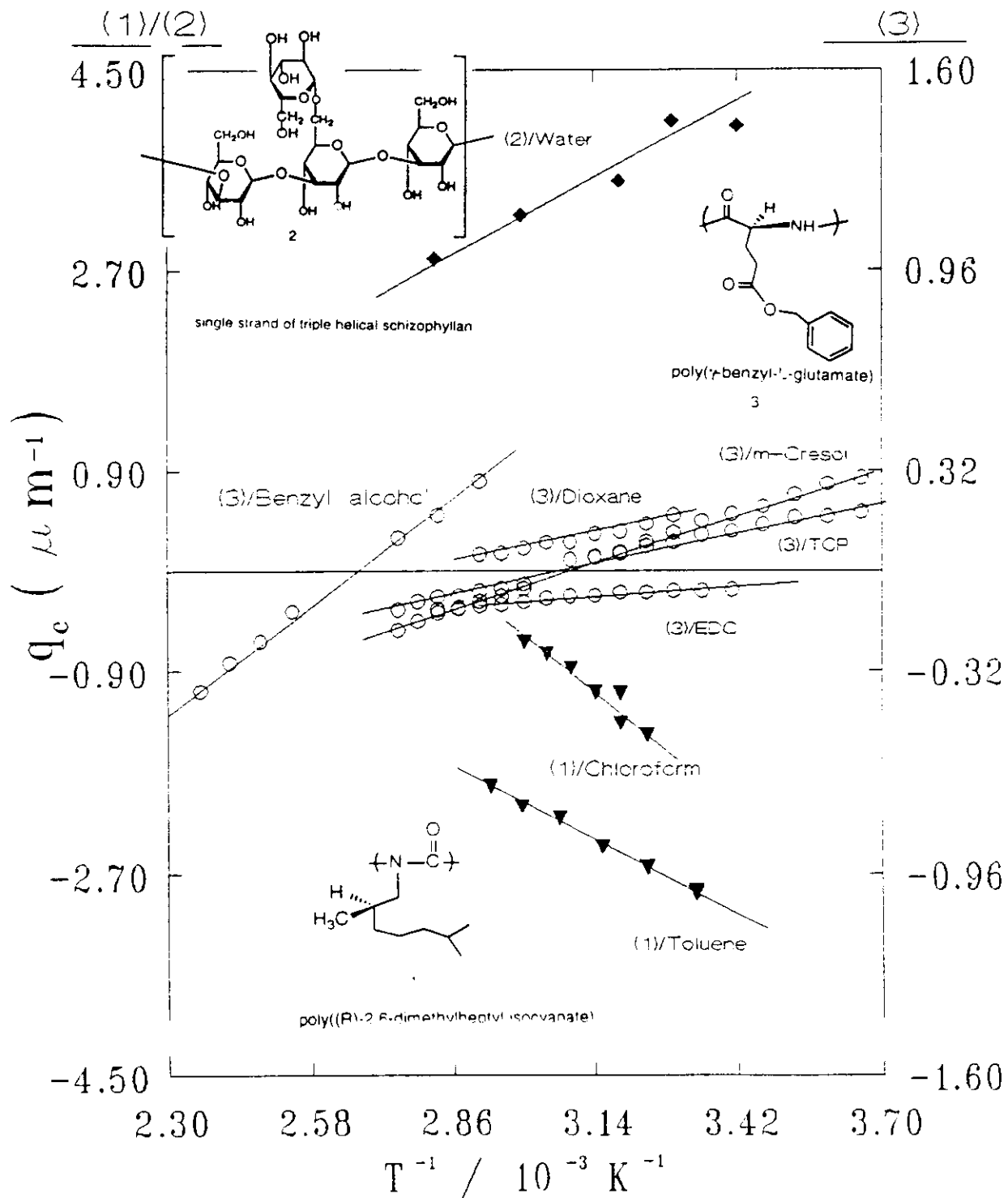
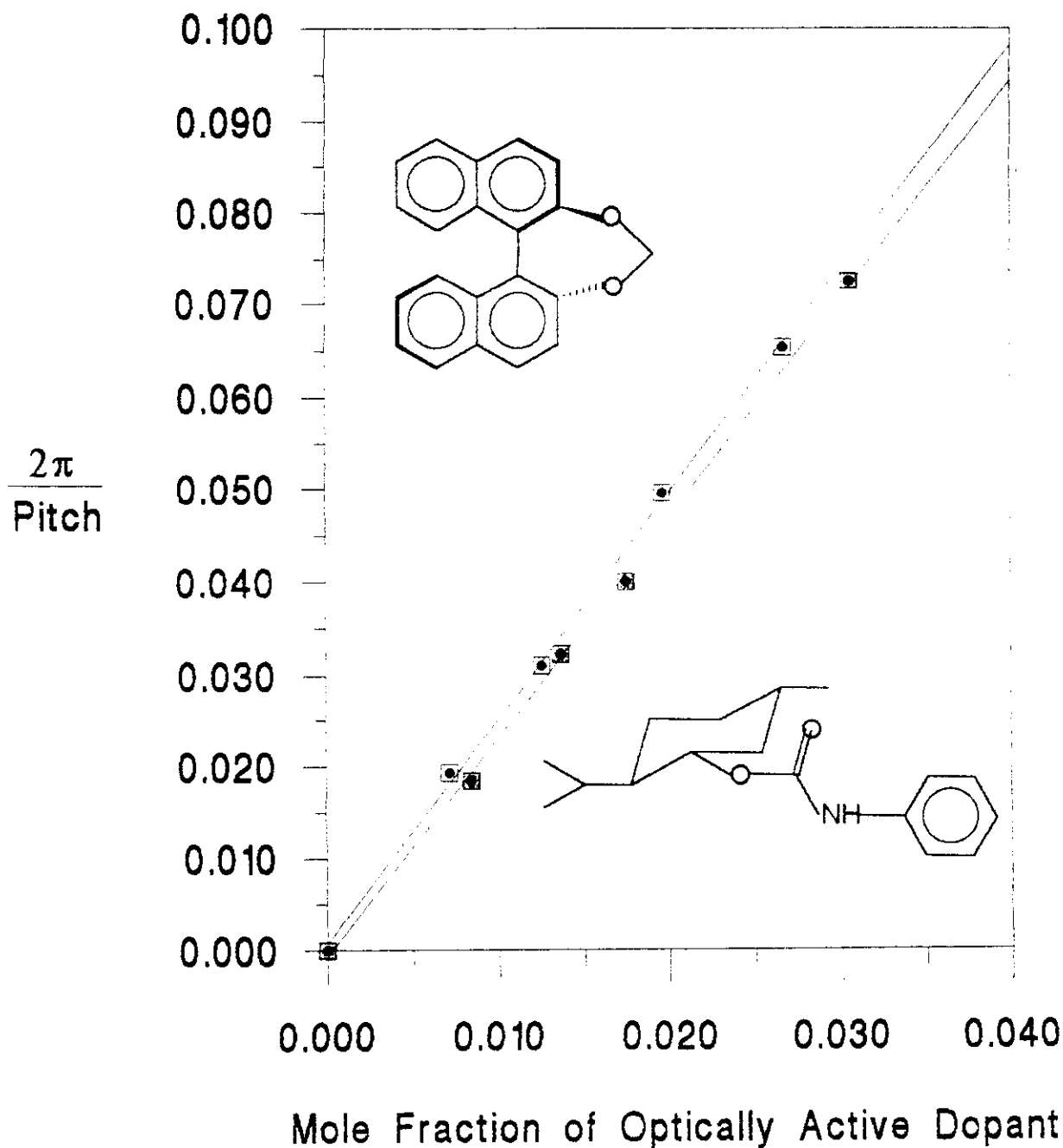


FIG. 3. Geometry of two threaded rods. The upper rod may approach the lower most closely if its principal axis is rotated clockwise with respect to the axis of the lower.

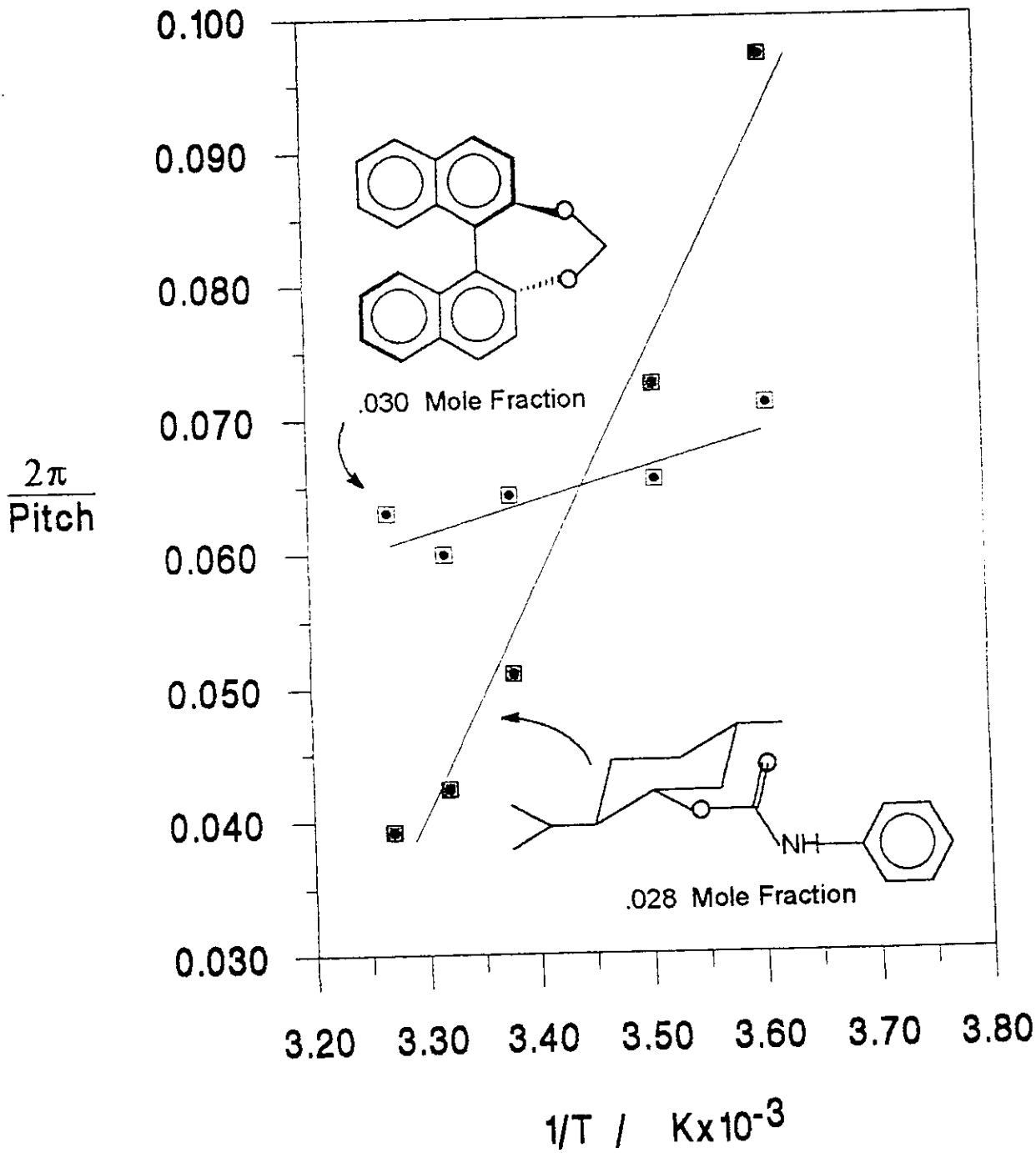
Cholesteric Wavenumber versus Inverse Temperature for Three Helical Mesogenic Macromolecules



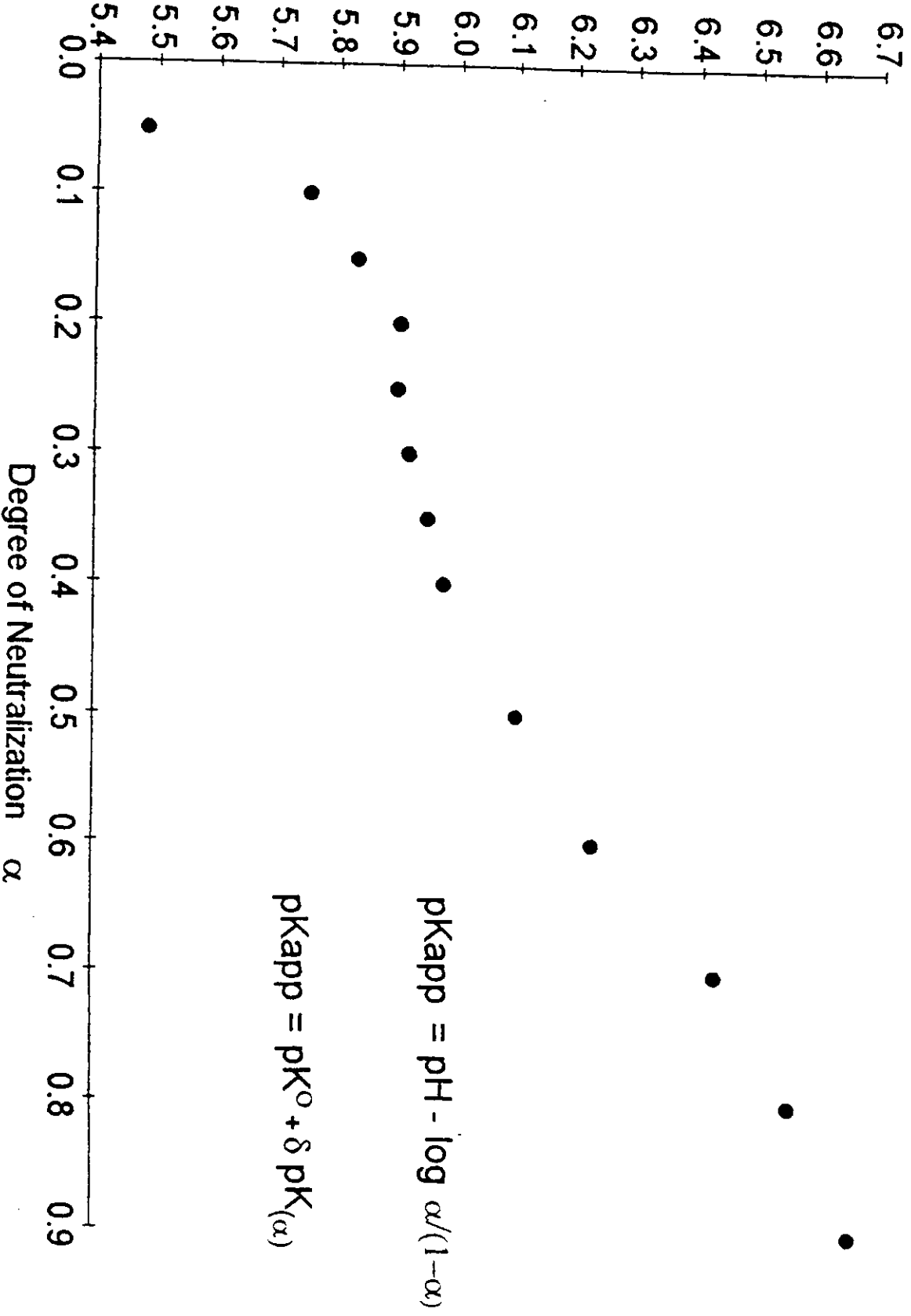
Cholesteric Pitch Wavenumber ($2\pi/P$) vs. Concentration at 12°C for Two Optically Active Molecules Added to The Lyotropic Phase of Poly(n-hexylisocyanate) in Toluene

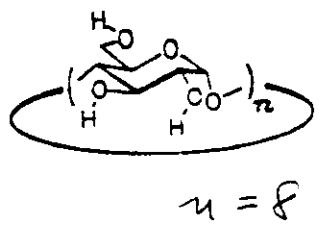
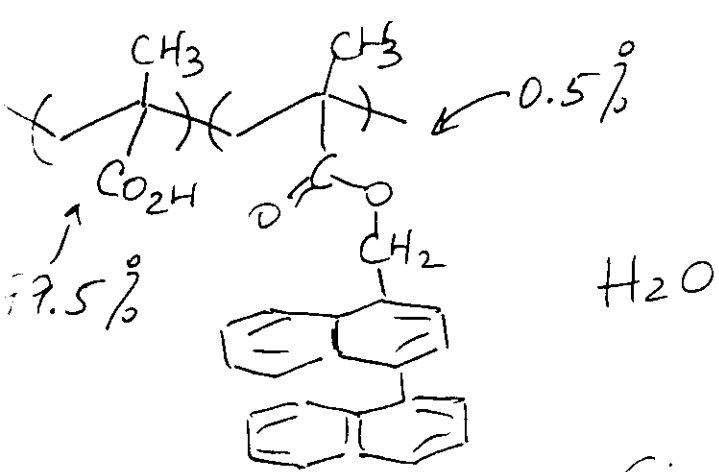


Cholesteric Pitch Wavenumber ($2\pi/P$) vs. Temperature for Two Optically Active Molecules Added to the Lyotropic Phase of Poly(n-hexylisocyanate) in Toluene

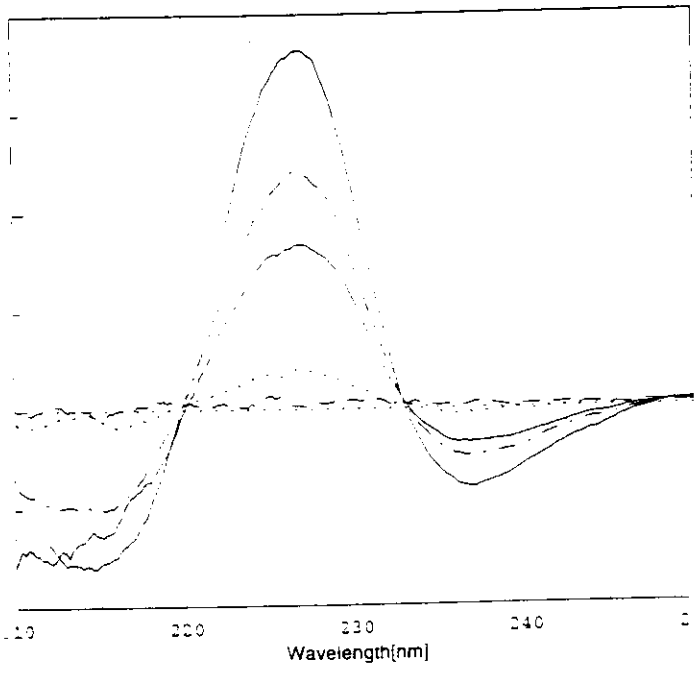


**pKapp for Labelled PMA
@ 0.072 M KCl**





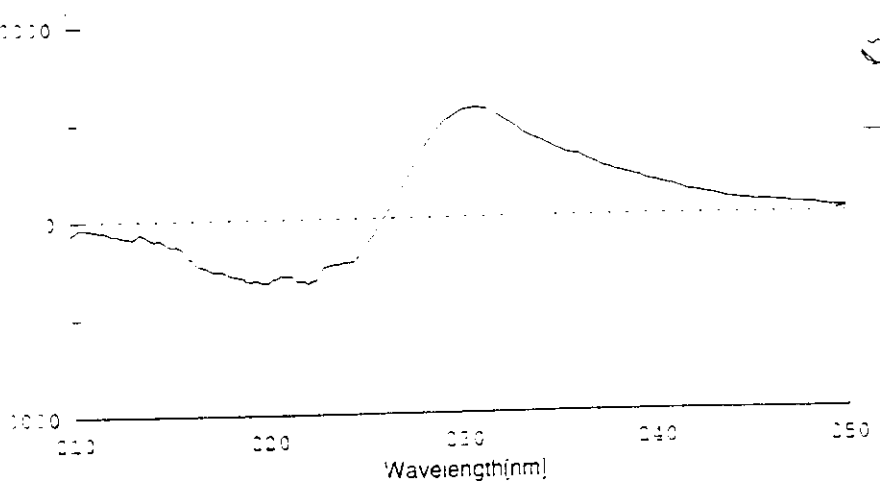
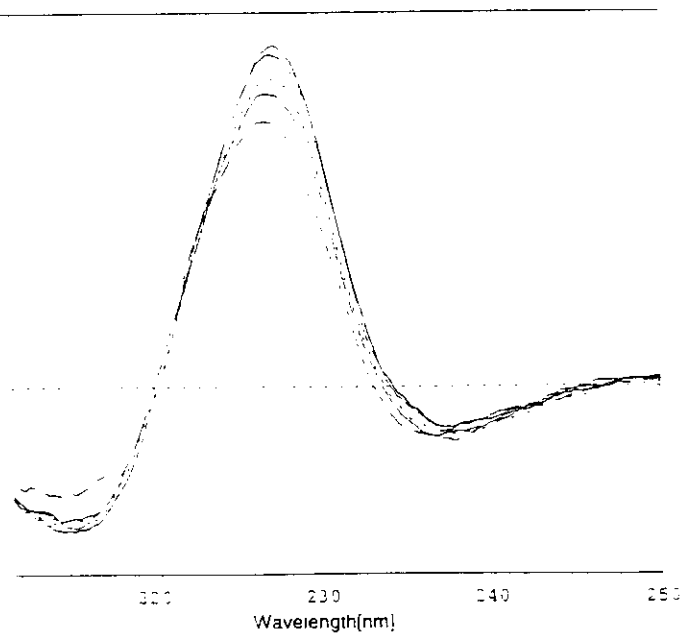
Circular Dichroism (CD)

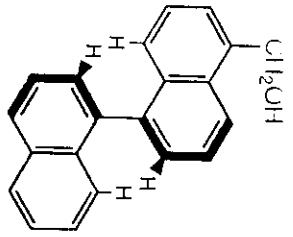
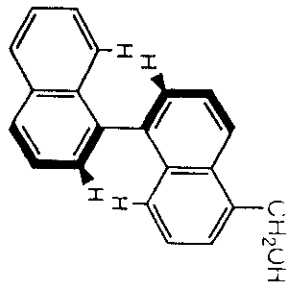


$\leftarrow \text{CD} = f(\text{pH})$

$\leftarrow \text{CD} = f(\text{time})$

remove α -cyclodextrin

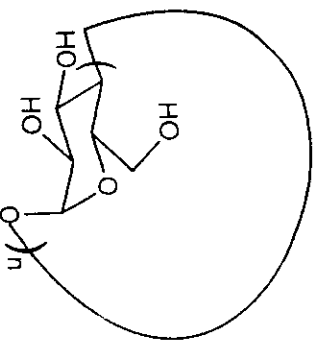
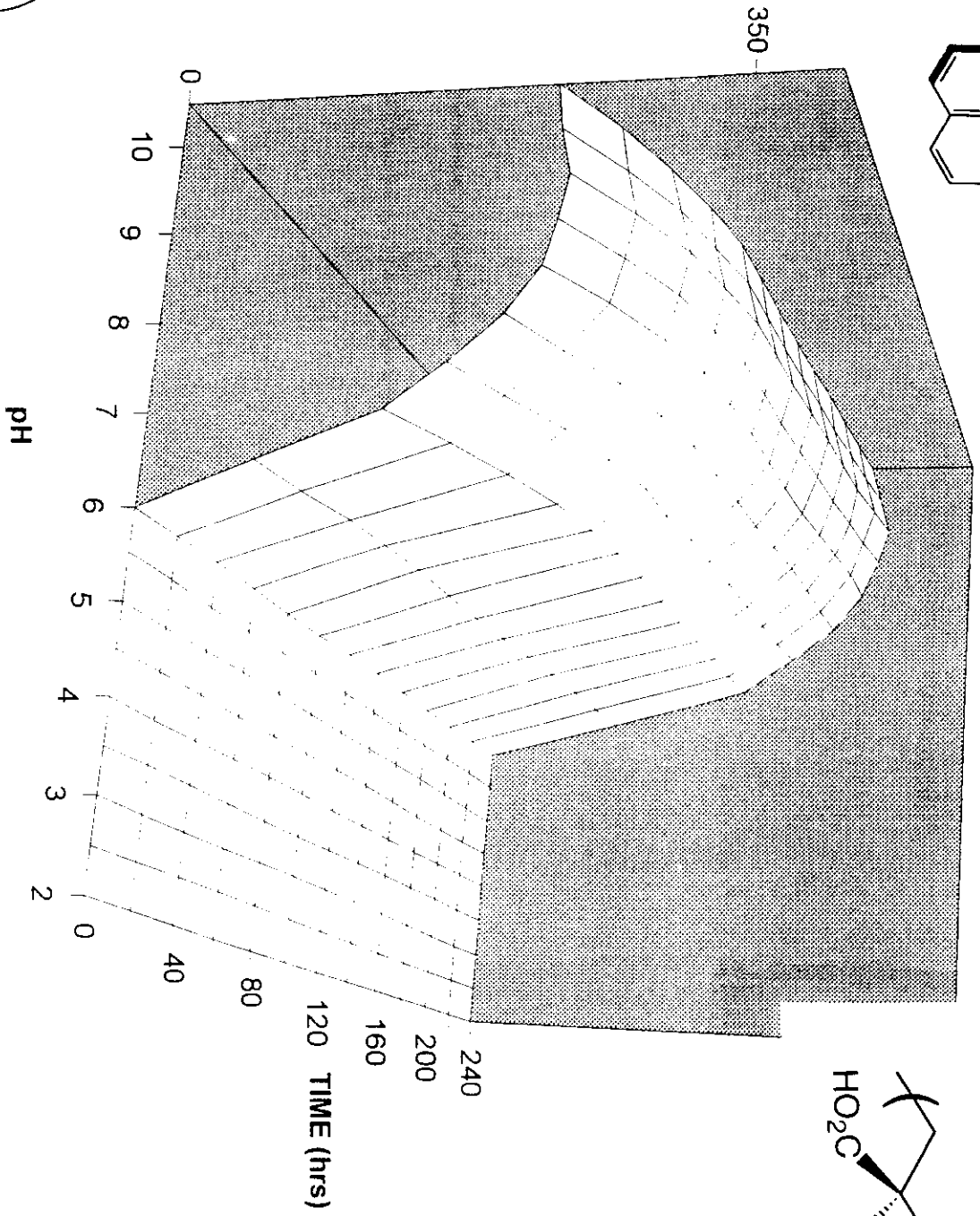


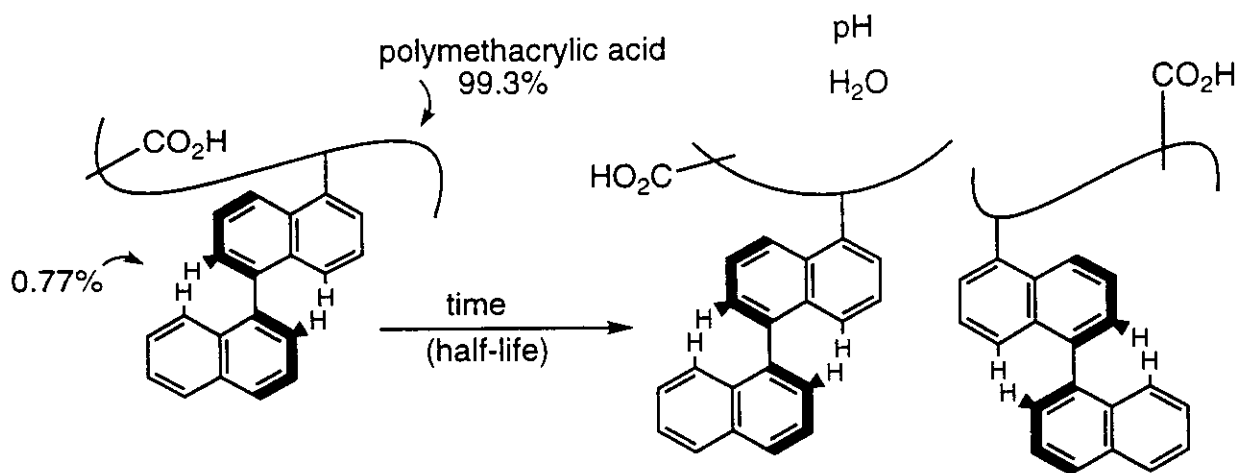


H_2O

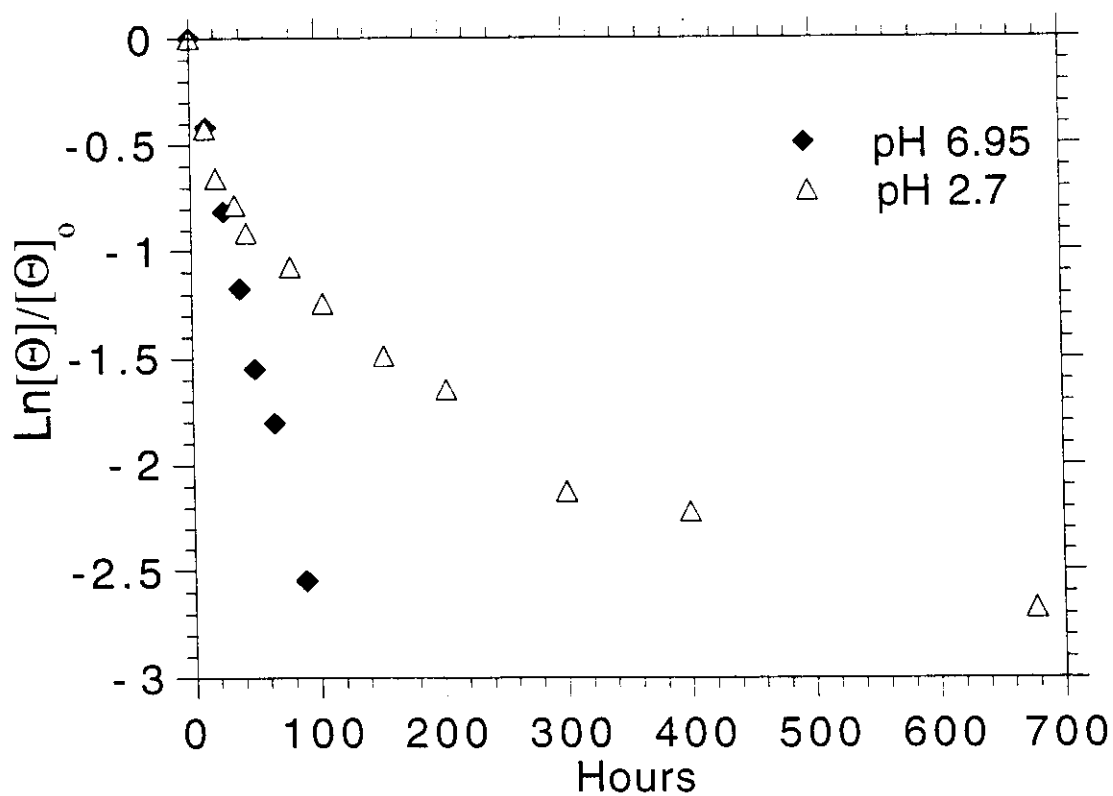


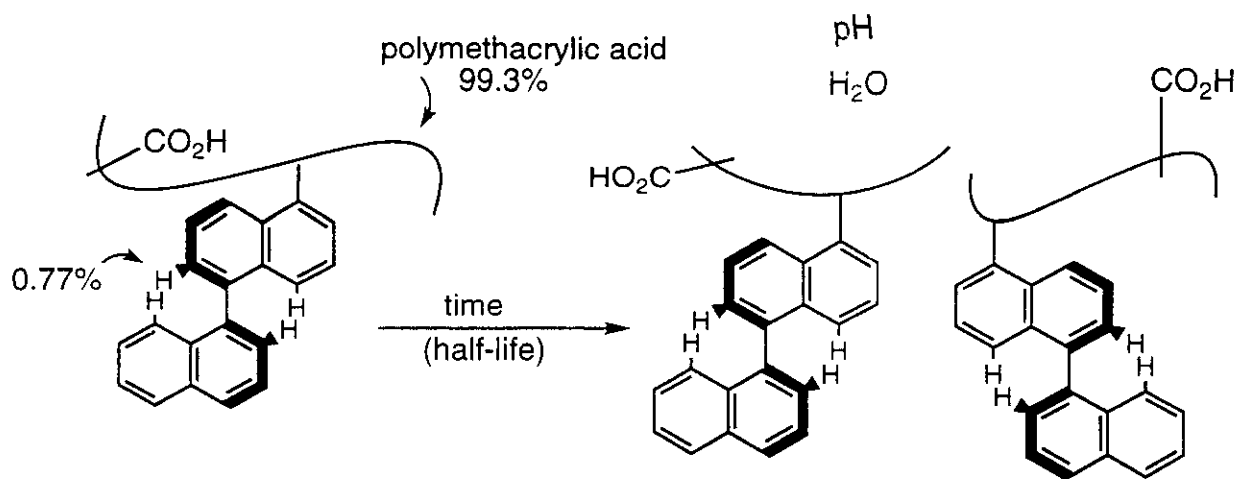
MOLAR ELLIPTICITY
(degrees cm mol)





First Order Plot of Racemization of Binaphthyl Labelled PMA





pH	Fraction CO ₂ H groups ionized α	Approximate half-life			
		t = 0	t = ∞		
		Fraction of racemization			
		first 40%	next 25%	next 15%	next 15%
2.7	<0.01	20	80	150	355
4.05	0.036	25	90	130	175
4.3	0.059	30	55	140	-
5.22	0.18	120	215		
5.45	0.25	~ 320			
6.1	0.5	~ 100			
6.95	0.75	19.3			
8.5	1.0	23.8			
BNA	-	22.9			
BNA*	-	~ 26			

BNA = Binaphthyl without polymer

* glycerol solvent, $\eta = 1020$ cp

[K⁺] = 0.072 M ; [CO₂H] = 0.014M ; [Binaph] = 0.0001M

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