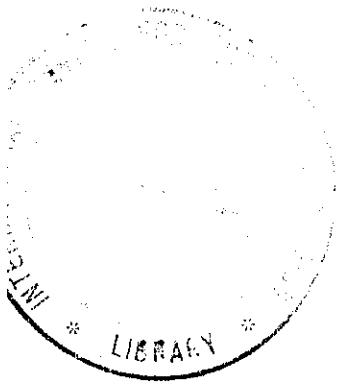

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SMR/206- 12

"SCHOOL ON POLYMER PHYSICS"

27 April - 15 May 1987

"LIQUID CRYSTAL POLYMERS"

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LIQUID CRYSTAL POLYMERS

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- Liquid crystalline order -

Low molar mass compounds with a strongly anisometric molecular shape or macromolecular compounds containing anisometric molecular sections may exhibit liquid crystalline order either in the bulk or in solution (1,2).

The essential structural feature that characterizes a liquid crystal phase over the other condensed states of the matter is the absence of any kind of long range order but the orientational order. This means that the orientations of the molecules (or of sections of them for polymeric substances) are more or less strictly correlated over a considerable distance compared to the molecular dimension. This feature discriminates a liquid crystal phase from the ordinary crystal phase which is characterized by long range positional as well as orientational order in 3 dimensions and from plastic crystals that preserve only long range 3-d positional order but lack orientational order. On the other hand, the absence of any kind of long range order is peculiar to the amorphous phase.

- Liquid crystal phases -

The study of the structure of the liquid crystalline state is a "work in progress" and quite a number of structurally different phases are known (3).

Dealing with polymeric materials, the nematic, smectic-A and smectic-C phases are the most commonly encountered. To sketch their structural peculiarity let's assume that the molecules, or the molecular sections of a polymer chain, have rod-like shape.

The nematic phase (N) is characterized by the molecules packing together in large assemblies with their long axis roughly parallel to a preferred direction (nematic director). The molecular positions are otherwise uncorrelated but, possibly, in the very short range packing.

Nematogenic molecules posessing a chiral group produce a particular nematic phase (cholesteric) whose structure is further characterized by the helicoidal variation in space of the direction of the nematic director. A super-chirality is induced in the phase that is responsible for the peculiar

optical properties of the cholesterics.

The smectic A phase (SA) has a layered structure. Within each molecular layer , which may be considered as a two-dimensional liquid, the long molecular axes are aligned roughly parallel to a preferred direction which coincides with the normal to the layer. The layer thickness is strictly related to the full length of the molecule. The SA phase, as well as the nematic one, is optically uniaxial.

The smectic C phase (SC) has also a layered structure but within each layer the preferred molecular orientation is tilted with respect to the normal to the layer. The layer thickness is shorter than the full molecular length. The SC phase is optically biaxial.

Other smectic phases, all characterized by having a layered structure, are known which exhibit in the short range higher degrees of order, also in 3-dimensions.

A peculiar kind of mesomorphism is the discotic one (4). It is structurally characterized by the presence of sets of disk-shaped molecular groups stacked in columnar piles which may pack together in a fairly regular two-dimensional array. Quite recently discotic mesomorphism has been reported to occur also with polymeric compounds (5).

- Detection and characterization of liquid crystallinity -

The polarizing microscopy (optical properties), the Differential Scanning Calorimetry (thermal properties) and the X-ray diffraction (structural properties) are the most immediate techniques that may be utilized to detect the occurrence of liquid crystallinity in polymers and to characterize the nature of the liquid crystal phase. None of these experimental techniques can be utilized alone without risks:

- Real liquid crystalline phases may occur with optically isotropic morfology (omeotropic texture)
- Optical anisotropy may be induced by mechanical stress on structurally amorphous materials
- Many liquid crystalline polymers containing the mesogenic groups in side chains are structurally amorphous when obtained by solution precipitation
- A double DSC endothermic signal does not necesserely imply the occurrence of melting of the crystal phase to a liquid crystal phase and successive isotropization of the latter. Solid phase transition or pre-melting crystallization, for example, may produce similar DSC curves.
- The X-ray diffraction pattern of a nematic phase is not easily distinguishable from that of a structurally amorphous

one.

Others experimental techniques based on the analysis of the peculiar dynamic properties which particularly characterize the nematic phase under the action of a magnetic or electric force field (1) are of less immediate applicability with the polymeric materials, especially for high molecular weight polymers in the bulk.

The study of binary mixtures with a low molecular weight component of known liquid crystal properties has been also utilized to characterize the nature of the liquid crystal phase exhibited by a polymer. Various spectroscopic techniques, particularly ^{1}H-NMR and ^{2}H-NMR, are of considerable help for the determination of the degree of order characterizing the mesophase (6-8).

- Chemical structure and liquid crystal properties -

Rod-like molecules

High molar mass, highly rigid and linear molecules are not likely to exhibit liquid cystal properties in the bulk because of their untractable melting temperatures. However their mesogenic character may show up, even at room temperature, in solution.

The theoretical base for the occurrence of liquid crystalline order in such binary systems has been discussed since long time by Onsager (9) and by Flory (10,11).

In the early Flory's treatment a very elementary structural parameter, the length to diameter ratio (axial ratio) of the rod-shaped macromolecule, and a single solute-solvent interaction parameter are sufficient to work out the conditions for the formation of anisotropic solutions as a function of the concentration.

Real systems such as poly-(p-phenylenterephtalamide)/sulfuric acid have been examined to the purpose (12).

The rigid-rod approach is also applicable to solutions of such polymers as poly-(γ-benzyl(L)glutamate) (13). In this case the rigid-rod is a large macromolecular section in helical conformation.

Mesomorphism has been observed in concentrated solutions of polyribonucleotides (14). Extensive studies are under way on the mesomorphic behaviour of cellulose derivatives in solution (15,16)

A theoretical treatment of liquid crystalline order in the bulk for rod-like molecules (also applicable ,however to semiflexible polymers whose macromolecules are taken as a sequence of Kuhn segments) has been developed by Flory and Ronca (17,18). (Actually, the early Flory's treatment contains the athermal case for the pure polymer as an

extrapolation to polymer volume fraction 1 of the general polymer/solvent system).

The Flory-Ronca thermal treatment contains two intrinsically relevant parameters, namely the axial ratio of the rigid molecular segments to express their steric hindrance and the $\Delta\alpha$ parameter (difference between the dielectric polarizability along and normal to the molecular long axis) to evaluate the energy of the intermolecular interaction. Figure 1 shows a calculated dipendence of the orientational order parameter (see pag. 5 for a definition of order parameter) on the temperature and on the axial ratio

Semiflexible polymers

Macromolecules exhibiting thermotropic liquid crystallinity in the bulk (i.e. in the melt) have molecular structures that substantially move away from the oversimplified rigid rod model (19 - 23). Although rigid, elongated (more generally, anisometric) molecular sections are normally preserved, they are connected together by atomic groups that allow the molecules to be more or less flexible or decrease the tightness of the molecular packing or reduce amount and perfection of the crystalline phase decreasirg melting temperatures to tractable levels.

The mesophasic properties depend on such molecular features as :

- length, chemical nature and rigidity of the "mesogenic rigid grcup"
- length and chemical nature of the flexible "spacer" connecting two mesogenic groups
- chemical nature of the atomic group connecting flexible spacers to rigid groups
- molecular weight and, for low molecular weight compounds, including polymers, nature of the chain termination
- composition and co-monomer sequence for copolymeric substances

The most basic influence of the above mentioned parameters may be on the very nature of the mesophase.

Figure 2 shows the influence of the length of the flexible parts on the liquid crystal phase for a series of "dimeric" model compounds. The smectic phase is favoured for short spacers and long terminal tails. The figures refer to compounds exhibiting both smectic and nematic mesomorphism and represent the ratio between smectic-nematic and nematic-isotropic molar transition entropies (24).

Figures 3-5 report the basic data concerning the liquid crystal properties of some linear polymers. The occurrence of nematic or smectic mesomorphism within comparable ranges of temperature (or no mesomorphism whatever) is connected to apparently subtle stereochemical differences whose role is not entirely understood (21,25-30).

A typical influence of the stereochemical nature of the flexible spacer is the fluctuation of the thermodynamic quantities connected to the isotropization of a nematic phase known as "odd-even effect".

Figure 6 shows the molar isotropization enthalpy as a function of the number of carbon atoms contained in the flexible spacer of a set of polymeric or "dimeric" homologues exhibiting nematic mesomorphism. As a reference, the analogous quantities for the "monomeric" compounds are reported (31 - 33).

Figure 7 shows the drastic influence on the odd-even fluctuation of changing the nature of the chemical group linking flexible spacer to rigid section of dimeric and polymeric homologues (33).

In the examples reported above the "even" members of the series exhibit higher values of the transition enthalpies (the same is true for entropies and transition temperatures) than the "odd" ones. Figure 8 shows a case when the reverse occurs (26).

Both cases have been discussed (34,35) and clarified to some extent taking into consideration the relationship between accessible conformations and linearity of the molecules.

The odd-even fluctuation of the thermodynamic quantities is paralleled by a similar fluctuation of the order parameter. This may be defined, for an assembly of rod-like molecules, by the formula $S = (3\cos^2\omega - 1)/2$ ω being the angle that the long molecular axis makes with the nematic director.

The determination of the order parameter for polymers and model compounds has been performed utilizing several experimental techniques such as IR dicroism, magnetic susceptibility, X-ray diffraction and, best of all, ^{1}H-NMR and ^{2}H-NMR.

A dependence of the order parameter on the temperature, which is a feature predicted by the "thermal" theories on liquid crystallinity, has been observed (36,37).

Copolymers

Most of the liquid crystal polymers of practical interest are copolymers. Actually, copolymerization offers a further powerful and versatile means to variate molecular structures to the purpose of regulating liquid crystal properties.

The most simple case is that of a random binary copolymer whose monomer units are both nematogenic (i.e. both parent homopolymers are nematogenic). The liquid crystal properties of the copolymer variate smoothly with composition. Isotropization temperature and molar isotropization entropy are close to the weighted average over the molar composition. In this respect, random copolymers behave like binary mixtures of low molecular

weight nematogenic compounds (38).

If one of the monomer units has a chiral center, the nematogenic copolymer exhibits cholesteric properties. The cholesteric pitch variates with composition (39).

Notwithstanding the periodic (monodimensional) structure of the smectic phase, it has been found to be compatible to a considerable extent with the non periodic structure of a random copolymer (40,41). Figure 9 refers to a smectogenic copolymer whose monomer units, although chemically homologous, are of considerably different length. Nevertheless, a single smectic phase appears whose periodicity changes regularly with composition.

Figure 10 on the contrary, shows data for a copolymer whose monomer units are quite different both by chemical nature and by length. The smectic mesomorphism is exhibited throughout the entire range of compositions but with two different smectic arrangements, characterized by a drastic change of the structural periodicity.

Virtually all the linear nematogenic polymers that have been studied for practical purposes have copolymeric structure. High-level mechanical strength at elevated temperatures is the quality most commonly looked for. This orients the chemical synthesis towards linear rigid-chain polymers whose chain rigidity and linearity has to be "spoiled" to some extent to allow thermotropic mesomorphism to show up.

Many molecular groups have been utilized to the purpose but by far the most extensively used are the terephtaloyl and the p-oxybenzoyl groups. These are contained in the first linear liquid crystal copolymer which appeared in the literature (20). Polyethyleneterephtalate modified by inserting 40 - 60% p-oxybenzoyl groups in the polymer chain exhibits nematic mesomorphism with a dramatic influence on such properties as tensile strength, elongation at breaking and melt viscosity (42), (Figure 11).

- Comb-like liquid crystal polymers -

A peculiar class of semiflexible liquid crystal polymers is characterized by having the rigid mesogenic groups inserted as side chain pendants (43-46).

A large variety of liquid crystal phases have been observed depending on the stereochemical nature of the mesogenic group.

A critical point appears to be the length of the flexible spacer connecting the mesogenic side group to the flexible main chain. Too short a spacer, coupling tightly the mesogenic group to the main chain, hampers the formation of the liquid crystal phase.

Provided an appropriate spacer has been inserted, the relatively high mobility of the mesogenic groups makes the comb-like polymers in the molten state behave to some extent like low molecular weight mesogens (for instance, the rigid groups may be easily oriented by magnetic or electric force fields).
This quality and the possibility, typical of their polymeric structure, of quenching molecular order to room tempertaure makes comb like liquid crystal polymers interesting materials for electro- and magneto-optical applications.

Liquid crystal elastomers whose optical properties are drastically influenced by applied deformations have also been reported (47).

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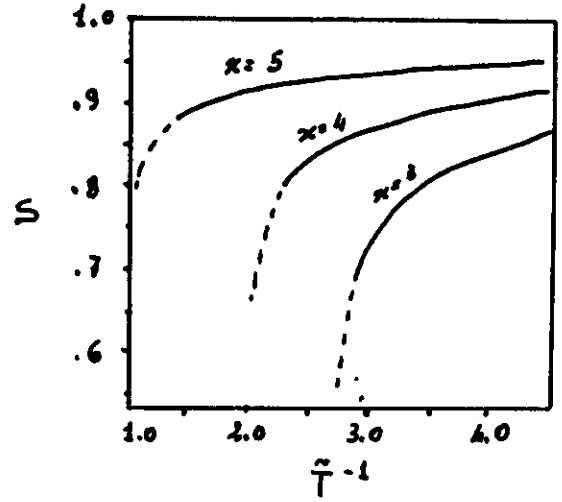
Fig.



S = order parameter

$\tilde{T} = T/x\cdot T^*$ $\left(T^* = \frac{(\Delta\alpha)^2}{K}\frac{zCz_c}{3r_0^6}\right)$

x = axial ratio

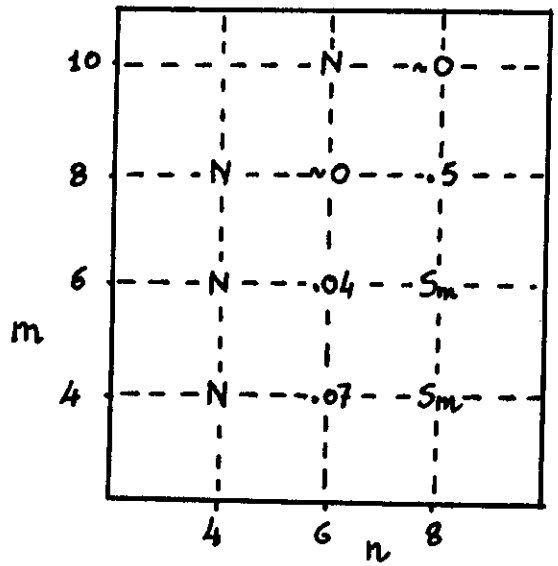
$\Delta\alpha = (\alpha_{\parallel} - \alpha_{\perp})$ dielectric anisotropy

K = Boltzmann const.

z_c = n° of first neighbours (lattice model)

r_0 = intersegmental distance for dense packing

Fig. 2



N = nematic

S_m = smectic

$\text{fig.} = \dfrac{\Delta S(S_m \rightarrow N)}{\Delta S(N \rightarrow I)}$

I = isotropic

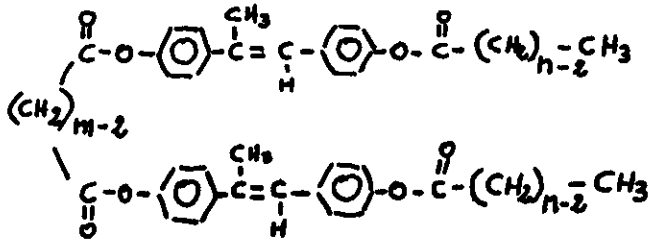
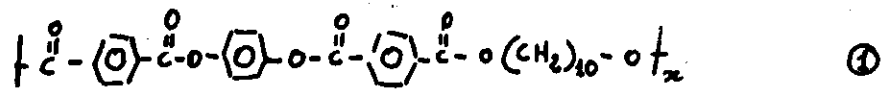
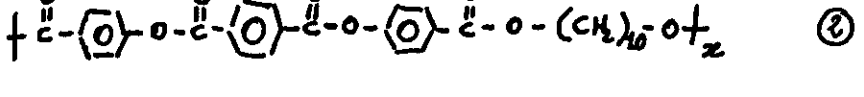


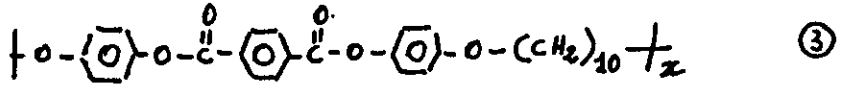
Fig. 3



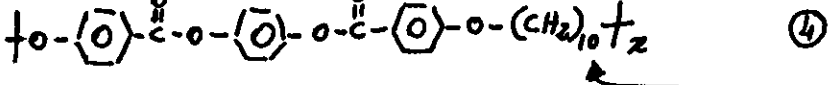
T_m = 231 °C T_i = 267 °C N



T_m = 220 °C T_i = 267 °C S_m



T_m = 265 °C T_i = 321 °C N



T_m = 236 °C T_i = 305 °C N

If = 12 S_m

① A.F. Zhu et al. 1983

② C. Obyr et al. 1982

③ S. Antoun et.al. 1981

④ L. Strzelecki et al. 1980

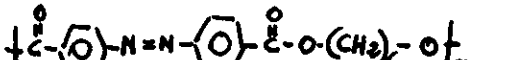
T_m = melting temp. T_i = isotropiz. temp.

Fig. 4


T_m = 245 °C
T_i = 325 °C
N
①


T_m = 209 °C
T_i = 329 °C
S_m
②


T_m = 245 °C
T_i = 300 °C
N
③


T_m = 268 °C
I


T_m = 190 °C
T_i = 267 °C
N
③

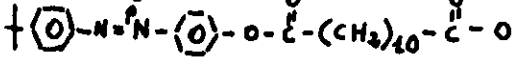

T_m = 218 °C
I

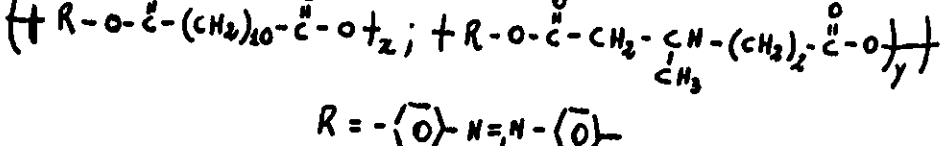
① D. Van Luyen et al. 1980

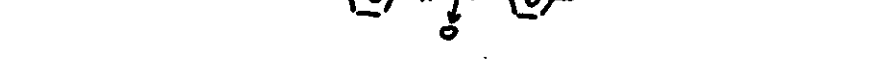
② P. Mauzac et al. 1981

③ K. Iimura et al. 1981

Fig. 5


T_m = 216 °C
T_i = 265 °C
N
(





x = .20 y = .80	T_m = 184 °C	T_i = 291 °C	Ch
x = .75 y = .25	T_m = 158 °C	T_i = 272 °C	Ch
x = .90 y = .10	T_m = 216 °C	T_i = 265 °C	N

Ch : cholesteric

① R. Blumstein et al 1982

② G. Mazet et al. 1981

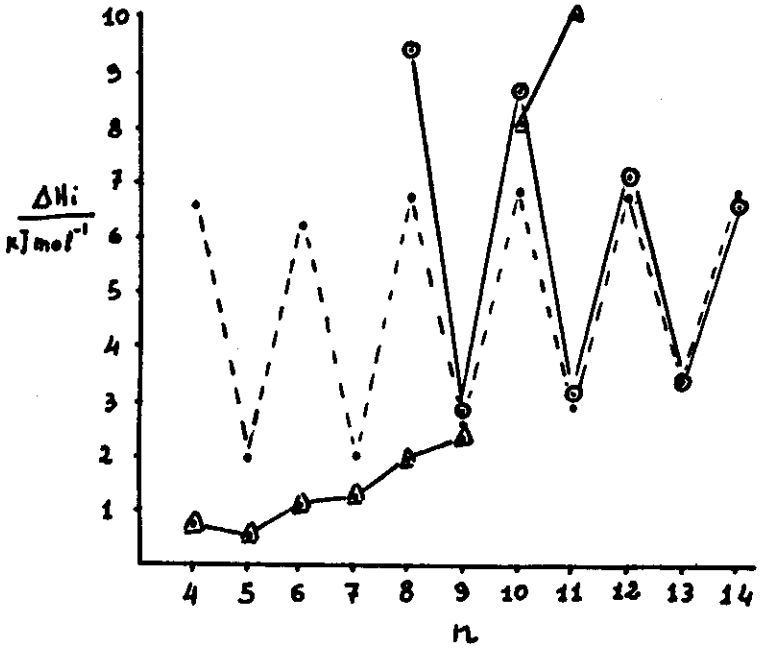
Fig. 6

○ $\{OOC-(CH_2)_{n-2}-COO-R\}_x$

• $CH_3(CH_2)_4COO-R-OOC(CH_2)_{n-2}-COO-R-OOC(CH_2)_4-CH_3$

△ $CH_3(CH_2)_{n-2}COO-R-OOC(CH_2)_{n-2}CH_3$

$R = -\langle O \rangle-\overset{CH_3}{\underset{}{C}}=\underset{H}{C}-\langle O \rangle-$



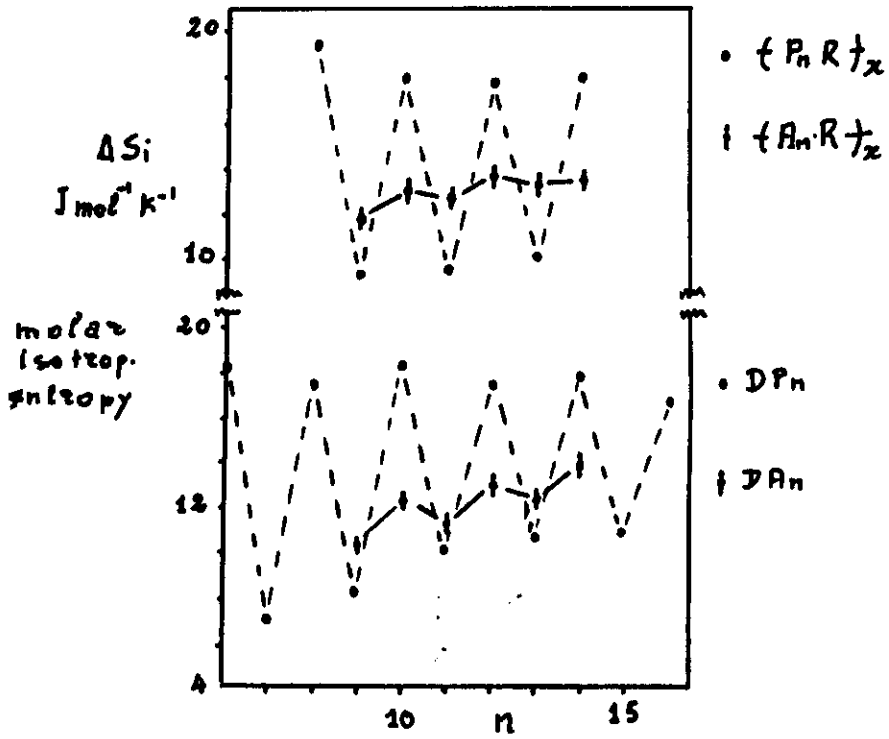
ΔH_i = molar isotropization enthalpy

Fig. 7

$2 = -O-\langle O \rangle-\overset{CH_3}{\underset{}{C}}=N-N=\overset{CH_3}{\underset{}{C}}-\langle O \rangle-O-$

$P_n = -\overset{O}{\overset{\|}{C}}-(CH_2)_{n-2}-\overset{O}{\overset{\|}{C}}-$

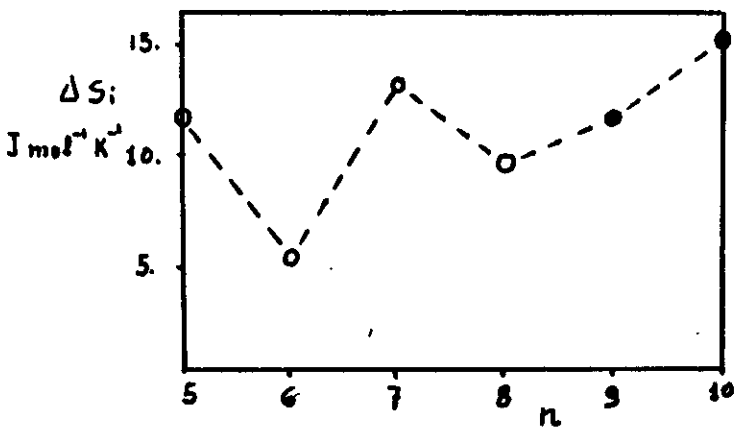
$DP_n = CH_3(CH_2)_4-\overset{O}{\overset{\|}{C}}-R-P_n-R-\overset{O}{\overset{\|}{C}}-(CH_2)_4CH_3$

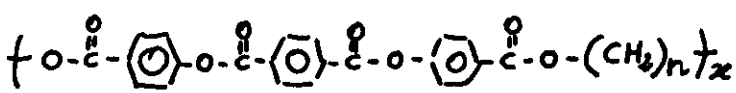


$A_n = -\overset{O}{\overset{\|}{C}}-O-(CH_2)_{n-4}-O-\overset{O}{\overset{\|}{C}}-$

$DA_n = CH_3(CH_2)_4-\underset{O}{\overset{\|}{C}}-R-A_n-R-\underset{O}{\overset{\|}{C}}-(CH_2)_4CH_3$

Fig. 8

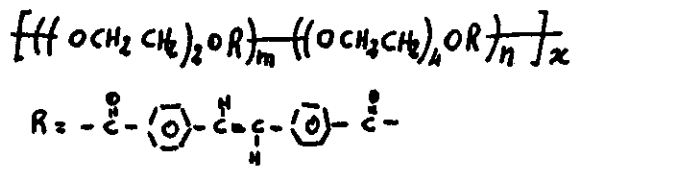


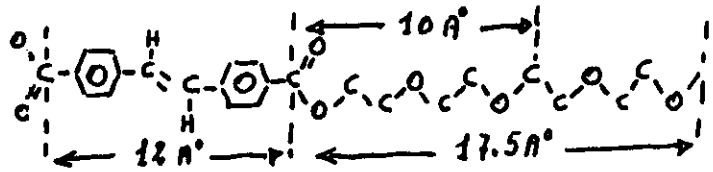


○ N

● Sm

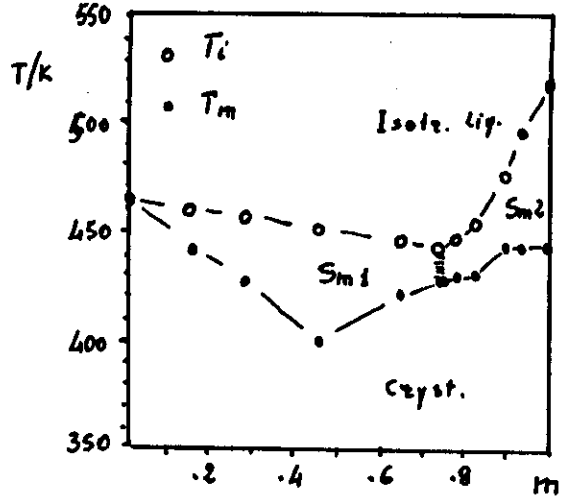
Fig. 9





m	Tm/K	Ti/K	ΔHi/kJ mol⁻¹	d/A°
0		368	3.2	22.3
14.4		403	3.4	21.9
50.0		428	3.6	21.3
75.0	416	468	4.0	19.7
100	438	519	6.3	17.8

Fig. 10



$$\left\{\left\{\text{O-CH}_2\text{CH}_2\text{-O-R}\right\}_m \left\{\text{O-(CH}_2\text{)}_{12}\text{-O-R}\right\}_{1-m}\right\}_x$$

$$R = -\overset{O}{\overset{\|}{C}}-\langle O\rangle-\overset{H}{\underset{|}{C}}=\overset{N}{\overset{|}{C}}-\langle O\rangle-\overset{O}{\overset{\|}{C}}-$$

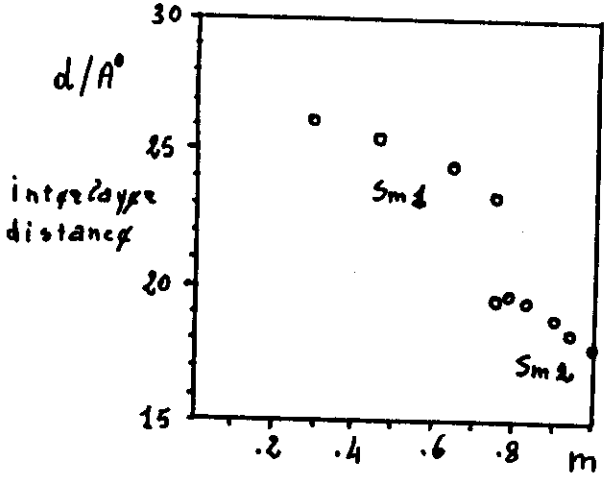
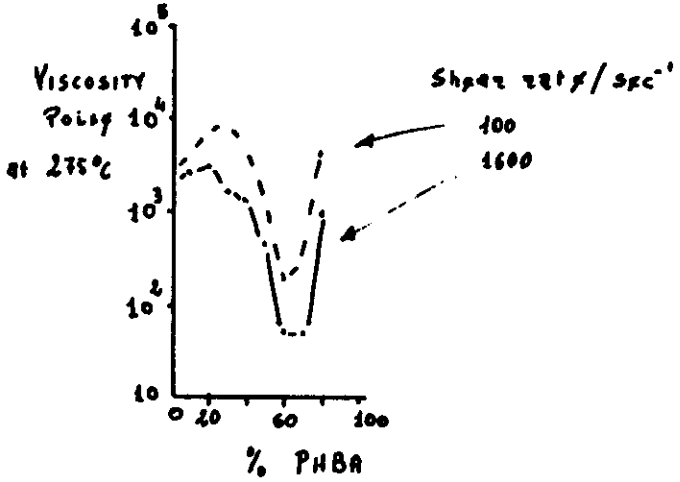


Fig. 11



$$\left\{\text{O-(CH}_2\text{)}_2\text{-O-}\overset{O}{\overset{\|}{C}}-\langle O\rangle-\overset{O}{\overset{\|}{C}}\right\}_{0.4}\left\{\langle O\rangle-\overset{O}{\overset{\|}{C}}-O\right\}_{0.6}$$

Tens. strength / MPa	237	(PET: 49.7)
Br. elong. %	9	(PET: 243)

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