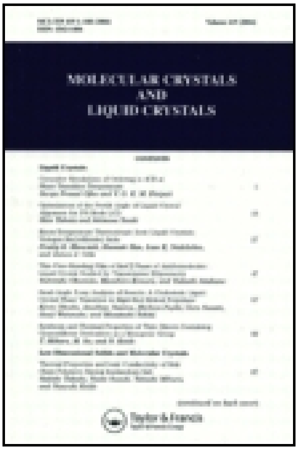

Molecular Crystals and Liquid Crystals

Columnar Phase in Main Chain and Comb-Like Polymers

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COLUMNAR PHASE IN MAIN CHAIN AND COMB-LIKE POLYMERS

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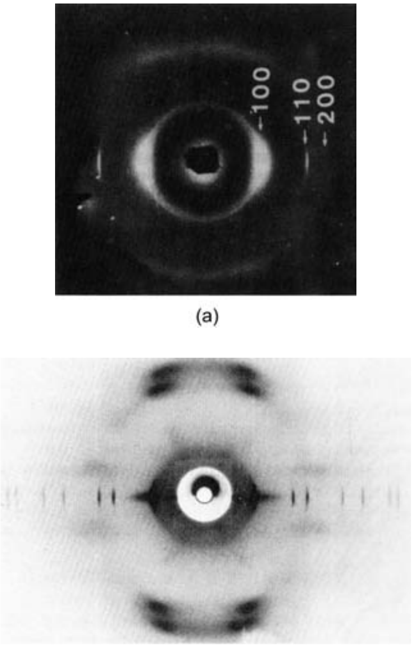
Thermotropic columnar phases are mainly associated with discotic or self-assembled polycatenar (multiple side-chain) mesogens. However, an important class of synthetic polymers, having no such mesogens or no traditional mesogens at all, also exhibit the hexagonal columnar phase. These range from main-chain staple polymers like polyethylene and Teflon to n-alkyl substituted siloxane, silane, phosphazene, peptide and cellulose polymers. A brief review is given with some details of phase behaviour of selected systems.

Keywords: hexagonal phase; polymer liquid crystals; rotator phase; polyethylene; poly(phosphazenes); poly(di-ethylsiloxane); poly(tetrafluoroethylene); mesophase.

Today we honour the 25th anniversary of the recognition of the columnar liquid crystal phase by Chandrasekhar and co-workers [1]. The phase was found in discotic molecules, and it has been and still often is referred to as the discotic phase. The columnar phase is described as a bulk phase possessing two-dimensional positional long-range order (LRO) [2]. Today a large class of compounds, including dendrimers, are known to exhibit the so-called self-assembled columnar liquid crystals [3,4,5] in which stratification into "discs" is not essential. It is not widely known in the liquid crystal community that a number of polymers with simple structure and no rigid "mesogens" whatsoever, let alone disk-shaped, form hexagonal columnar liquid crystals. Moreover, it is intriguing that this phase has been found in such polymers in early 1960's. However its recognition as a new phase type, a new state of order and a liquid crystal has been missed until long after 1977, and therefore the primacy of the discovery by Chandrasekhar, who recognised all these features, is not in question.

To the best of my knowledge, the first mention of a phase in polymers, referred to as "hexagonal crystal", but which we now know to be columnar liquid crystal, was the reference to the high-temperature modification in poly(*t*-1,4-butadiene) in a general paper on crystallography of polymers by

Natta and Corradini [6]. This phase, stable between 83°C and 164°C, was fully explored and reported 10 years later by Suehiro and Takayanagi [7] who still referred to it as crystalline. The first full report which clearly indicates the two-dimensional order in a hexagonal phase in polymers was that on the $>30°C$ modification of poly(tetrafluoroethylene) (Teflon) by Clark and Muus in 1962 [8]. Teflon has two truly crystalline modifications, one below 19°C and the other between 19°C and 30°C, with two different regular helical conformations. Above 30°C the long range order in the chain direction is lost, the helicity is only short range and frequent helix reversals occur. The diffraction pattern is shown in Figure 1a. This phase is stable up to the "melting point" (isotropization point) of Teflon, which is around 330°C. A section of the 13/6 helical polymer chain is shown in Figure 2, from which the approximately cylindrical van der Waals envelope of the chain is apparent. It is easy to imagine that translational disordering along the chain axis could occur at sufficiently high temperatures, leading to the



(a)

(b)

FIGURE 1 X-ray diffraction patterns of polymer fibres: (a) poly(tetrafluoroethylene) at 31°C [8], (b) linear polyethylene at high pressure (>4 kbar) and temperature [29]. In both cases the fibre axis is vertical. Sharp reflections are observed only on the equator, while all non-equatorial scattering is diffuse (reproduced by permission of Marcel Dekker Inc.).

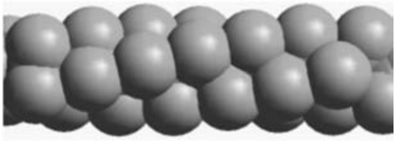


FIGURE 2 A section of the 13/6 helix of poly(tetrafluoroethylene) in the low-temperature (<16°C) crystalline phase.

loss of interchain register and a consequent inevitable loss of intramolecular order.

Polyethylene, unlike Teflon, crystallizes in a planar zigzag conformation (2/1 helix) and forms crystals with an orthorhombic unit subcell like that of longer n-paraffins. However, at pressures above 4 kbar polyethylene transforms into a hexagonal phase before melting [9]. Fibre diffraction pattern of this phase is shown in Figure 1b [29]. It again shows sharp Bragg equatorial and diffuse non-equatorial scattering, consistent with the assignment of the structure as columnar liquid crystal. In all current examples the column cross-section contains only one chain, hence its diameter is of the order of 4–5 Å, considerably less than that in discotics.

A phase related to hexagonal phase in polyethylene is the "rotator" phase observed below the melting point in *n*-alkanes between $C_{11}H_{24}$ and $C_{40}H_{82}$ [10]. This is an orientationally-disordered crystalline phase (sometimes referred to as plastic) in which the molecular chains have a minimum of 4 equivalent orientations around their long axis, giving rise to either a centred orthorhombic or a hexagonal lattice [11,12], or a tilted pseudo-hexagonal lattice in the case of longer alkanes [13]. It had been thought that the rotator phase in paraffins and the hexagonal phase in polyethylene are unconnected, partly because in the former the chains are conformationally ordered while in the latter they are significantly disordered. Furthermore, the rotator phase disappears with increasing pressure while the polyethylene phase only appears at high pressure. From Clapeyron equation it follows that the former situation (convergent phase boundaries) occurs when [14]

$$\frac{s_h - s_o}{s_m - s_h} < \frac{v_h - v_o}{v_m - v_h} \tag{1a}$$

while the latter (divergent boundaries) occurs when

$$\frac{s_h - s_o}{s_m - s_h} > \frac{v_h - v_o}{v_m - v_h} \tag{1b}$$

Here *s* and *v* are specific entropy and volume, and subscripts *o, h* and *m* refer respectively to the orthorhombic crystal, hexagonal columnar and melt phases.

There is of course the difference between the alkane rotator phase and the polyethylene phase in that the former is a 3-d crystal owing to the finite length of chains and the uniform layer stacking. However, in all other respects it was shown that the two phases are in fact manifestations of the same master structure with properties changing continuously as a function of temperature [15]. Figure 3 is a compilation of pressure-temperature diagrams for a series of alkanes and polyethylenes. The alkane p-T data, taken mainly from [16], show a diminishing convergence with increasing

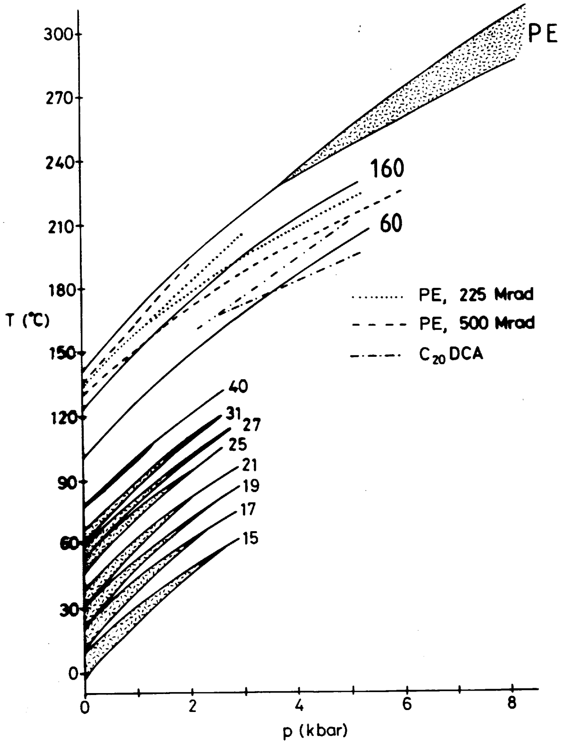


FIGURE 3 Pressure-temperature diagram of a series of normal alkanes C_nH_{n+2} (*n* is indicated) and polyethylene (PE), with the shaded area indicating the region of the rotator phase and the hexagonal columnar phase, respectively. Hexagonal phase boundaries are also shown for polyethylene γ-irradiated with 225 and 500 Mrad, as well as for 1,20-di-eicosanoic acid $HOCO(CH_2)_{18}CO_2H$. Below and above the rotator/hexagonal temperature range are, respectively, orthorhombic crystal and isotropic melt (from [15] by permission of American Chemical Society).

chain length, so that for $C_{40}H_{82}$ the boundary lines are nearly parallel. The phase is then lost for longer alkanes, but reappears in polyethylene at higher temperatures. Bridging the gap is polyethylene exposed to ionizing radiation. Irradiation was found to bring the triple point down to below atmospheric pressure [17,14]. This allowed the use of IR spectroscopy for quantitative determination of g^+ tg^- kinks, the dominant conformational defects in the hexagonal phase. The number of g^+tg^- defects per 100 C–C bonds is plotted as a function of temperature in Figure 4 for the rotator phase of several *n*-alkane systems and for the columnar phase in irradiated polyethylene. The steady increase in c_{kink} is consistent with the continuous change in character of the phase from "low-entropy" (Eq. (1a)) to "high-entropy" (Eq. (1b)) and the consequent change in phase boundaries from convergent to divergent in the p-T diagram (Fig 3).

A theoretical description of the columnar phase in main-chain polymers has yet to be devised. Qualitatively, a combination of rotational and conformational disorder is thought to be attainable with relatively low expense in intermolecular interaction energy since, due to the simple chemical

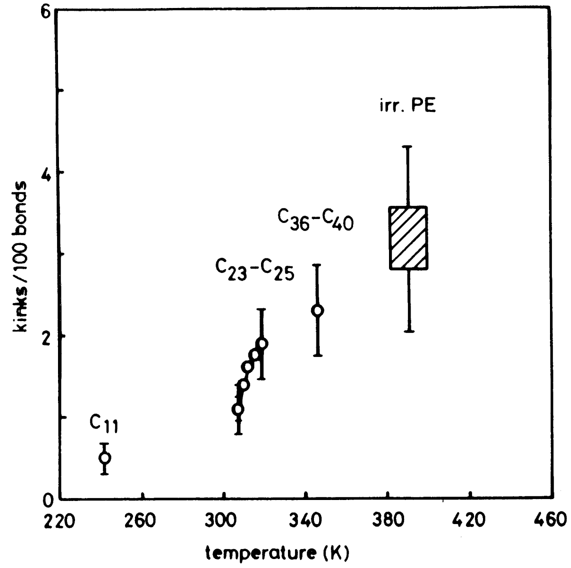
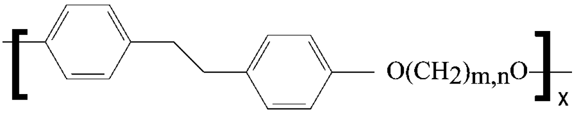


FIGURE 4 Concentration of g^+tg^- ("kink") conformational defects per 100 C-C bonds in the rotator phase of n-$C_{11}H_{24}$, binary mixtures of *n*-alkanes $C_{23}H_{48}$–$C_{25}H_{52}$ and $C_{36}H_{74}$–$C_{40}H_{82}$, and in the columnar phase of irradiated polyethylene. Alkane mixtures were used in order to widen the temperature range of the rotator phase (from [15] by permission of American Chemical Society).

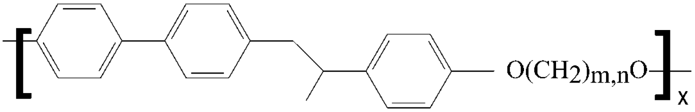
structure and high chain flexibility, nearest neighbour order could be maintained to a large degree in the columnar phase.

While conformational disorder breaks the chain periodicity in the columnar phase of simple polymers like polyethylene, poly(*t*-1,4-butadiene) and polytetrafluoroethylene, introducing chemical aperiodicity was shown to result in the Col_h phase in segmented copolymers. An example of the latter are random copolyethers BPE-*m,n* containing alkylene spacers with carbon numbers *m* and *n* differing by 4 or more [18]:



Thus while BPE-12 homopolymer and BPE-10,12 copolymer exhibit only crystalline phases, copolymer BPE-8,12 ($m = 8$, $n = 12$) displays the hexagonal columnar phase in the high temperature region. Figure 5 shows a series of X-ray powder diffractograms of BPE-8,12 recorded during cooling from isotropic melt, through the hexagonal columnar and into the Crystal-B phase. The Col_h–Cr_B transition is identified by the appearance of the small layer diffraction peak at low angles, coinciding with a small but sharp exotherm in the simultaneously recorded DSC thermogram. During this transition the strong 1 0 peak at 4.5 Å barely changes in either intensity or position, making this a true 2-d to 3-d ordering transition. The packing in the two phases is schematically depicted in Figure 6, where the dark and light segments represent the BPE and aliphatic moieties.

A further step in the development of main-chain columnar polymers was made by replacing one of the phenyl groups in the BPE unit with a biphenyl group, thereby extending the calamitic mesogen and making it more rigid. A methyl group was added to the ethylene unit to depress the melting point, resulting in the following family of copolymers, labelled TPP-*m,n*:



The idea was to obtain the calamitic nematic as well as calamitic columnar phase in one and the same polymer. The true 2-dimensional columnar phase was obtained only in copolymers where one of the spacers was even and the other odd, and where $|m-n| \geq 3$ [19,20,21,22]. When *m* is relatively small ($m < n$) and the *m* comonomer is in excess, TPP-*m,n* copolymers indeed show a high temperature nematic phase and the columnar phase at lower temperatures–see Figure 7.

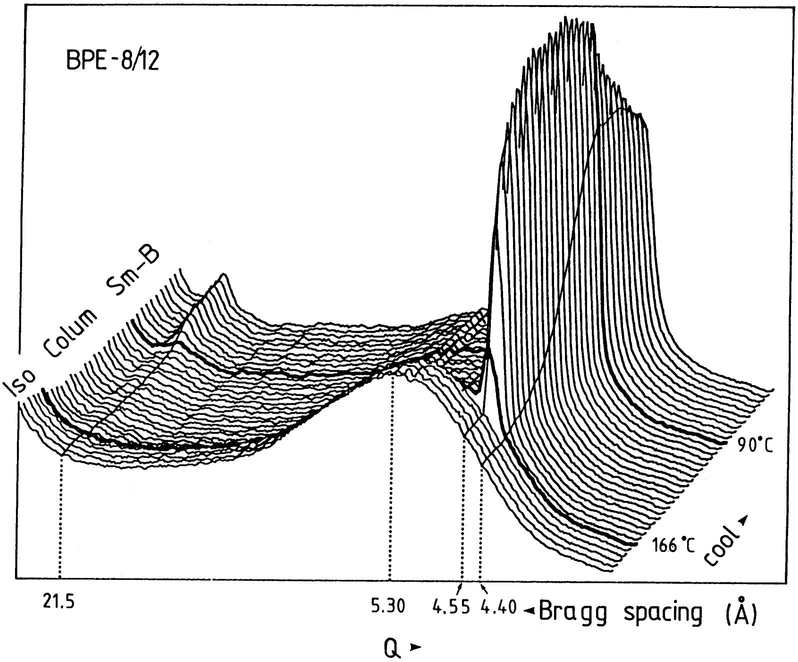


FIGURE 5 Series of powder X-ray diffractograms of copolymer BPE-8,12 (1:1 molar) recorded during cooling from the isotropic melt at 5°C/min. Bold spectra correspond to exotherms in the DSC traces recorded simultaneously (from [18] by permission of American Chemical Society).

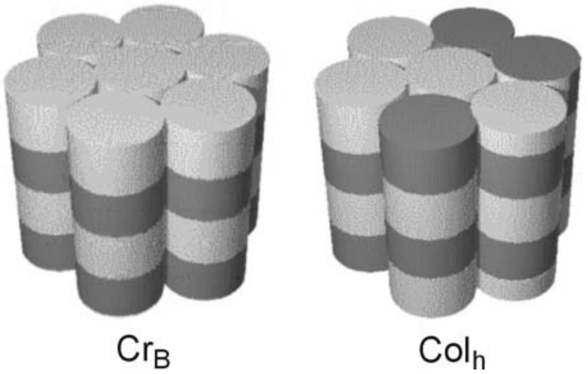


FIGURE 6 Schematic representation of Crystal-B and hexagonal columnar phases in segmented main-chain copolymers such as BPE-*m,n*. A polymer chain is represented by a cylindrical column. The mainly aromatic and the alkyl spacer segments are coloured differently.

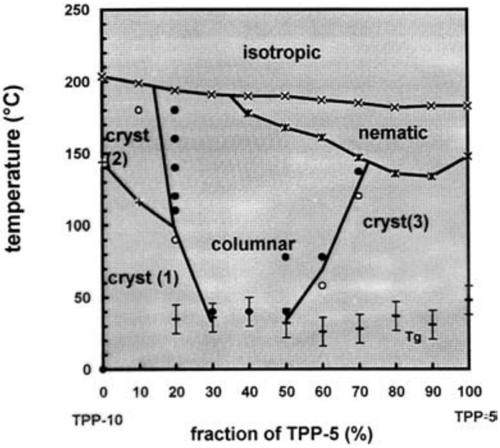
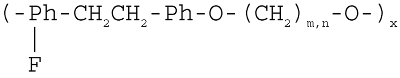
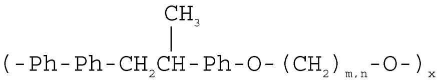


FIGURE 7 Transition temperature *vs.* monomer composition for copolyethers TPP-5,10. The crosses represent isotropization temperatures and the horizontal bars the glass transition temperatures, both obtained by DSC. Empty and full circles indicate, respectively, the crystalline and the columnar phase ascertained by X-ray diffraction [20].

The columnar phase has the unique ability to extend flexible polymer chains [23,24]. Normally, on direct crystallization flexible polymers form multiply folded-chain crystals, as the growth rate of such metastable crystals is the highest. The columnar phase uniquely has both the driving force and the mobility necessary to eliminate the folds. For certain applications, e.g. for high-modulus materials, it is desirable to extend the chains and the pathway *via* the columnar phase may be appropriate in some cases. The insertion of the nematic phase may serve to partially but rapidly pre-extend the chains, as extension directly from a random coil conformation is quite slow.

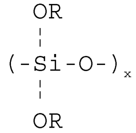
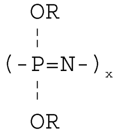
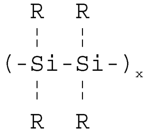
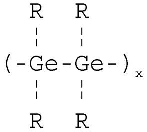
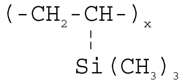
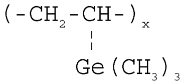
One promising application of the chain-extending property of the columnar phase is high-pressure annealing of ultra-high molecular weight polyethylene (UHMWPE) [25]. With molecular weights of several million, interdiffusion of UHMWPE molecules is so slow that the nascent polymer powder would not fuse on melting due to excessive chain entanglements. This reduces the fatigue resistance of UHMWPE implants used in artificial knees or hips, and causes fragments to break off the implants on prolonged use. Recent experiments with high pressure annealing of such products, utilizing the chain-extending and hence chain-disentangling property of the hexagonal columnar phase, have given promising results and commercial application is anticipated [26].

TABLE 1 Non-discotic Polymers Exhibiting a Thermotropic Hexagonal Columnar Phase

Polymer	Common name	Temperature interval (°C)	Ref.
A)			
polyethylene			
– at high pressure (triple point 3.5 kbar. 215°C)	anabaric hexagonal	280–307 (@ 8 kbar)	9, 28, 29
–constrained ultra-oriented fibres	ditto	155–180	30
–irradiated	ditto	60:130– 100:135′	17
PE with short branches: –ethylene-propylene copolymer	ditto	< 60	17
–ethylene-vinylchloride copolymer	hexagonal	< 20:54	31
1,4-t-polybutadiene $(-CH_2-CH=CH-CH_2-)_x$	Form II	83–164	6, 7
polytetrafluoroethylene $(-CF_2-CF_2-)_x$	Form I	30–330**	8
tetrafluoroethylene-hexafluoropropylene copolymer		> −40	32
polytrifluoroethylene $(-CF_2-CHF-)_x$		< r.t.−193:209	33, 34
vinylydene fluoride-trifluoroethylene copolymer (50–80% VDF)	paraelectric phase	70: 150–150:160	35
poly-p-xylylene $(-Ph-CH_2CH_2-)_x$	β_2	280–420	36
copolyethers of biphenylethane (BPE-m,n) $(-Ph-CH_2CH_2-Ph-O-(CH_2)_{m,n}-O-)_x$	columnar	104–181	18
fluorobiphenylethane (FBPE-m, n)  $(-\underset{F}{Ph}-CH_2CH_2-Ph-O-(CH_2)_{m,n}-O-)_x$ and BPE-FBPE copolymers		110–140	37
copolymers of 1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl) propane (TPP-m, n)  $(-Ph-Ph-CH_2\overset{CH_3}{CH}-Ph-O-(CH_2)_{m,n}-O-)_x$	columnar	50–200	19, 20, 21, 22

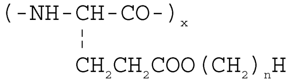
(Continued).

Table 1 Continued.

Polymer	Common name	Temperature interval (°C)	Ref.
B) polydialkylsiloxanes  $(-\overset{OR}{\underset{OR}{Si}}-O-)_x$ R=C_2H_5 through C_6H_{13}	α_m, μ, visco-crystalline	−50:+40− 50:200	38, 39, 40, 41, 42
polyphosphazenes  $(-\overset{OR}{\underset{OR}{P}}=N-)_x$ R=F_3C-CH_2, aromatic or alkyl	δ	150:180– 360:400	43, 44, 45, 46
polydialkylsilanes  $(-\overset{R}{\underset{R}{Si}}-\overset{R}{\underset{R}{Si}}-)_x$ R=$n-C_4H_9$ through $n-C_{14}H_{29}$	Phase II, columnar	10:80–$>$450	47, 48, 49
polydialkylgermanes  $(-\overset{R}{\underset{R}{Ge}}-\overset{R}{\underset{R}{Ge}}-)_x$ R=$n-C_8H_{13}$		$>$15	50
polyvinyltrimethylsilane**  $(-CH_2-\underset{Si(CH_3)_3}{CH}-)_x$			51
polyvinyltrimethylsilane  $(-CH_2-\underset{Ge(CH_3)_3}{CH}-)_x$			52

(Continued)

Table 1 Continued.

Polymer	Common name	Temperature interval (°C)	Ref.
C) poly-n-alkyl-L-glutamates  $(\text{-NH-}\underset{\substack{\vert\\ \mathrm{CH_2CH_2COO(CH_2)_nH}}}{\text{CH}}\text{-CO-})_x$	n < 8; "2-d hex."	40:130–200	
n = 4–18	n > 10: "Region B" n = 18: "columnar"	−24: +62 – 30:64	53, 54
-cellulose *tri-n*-alkanoates n = 8–18	columnar	60:90–100:120	55

[*] $T_{\text{crystal-columnar}}$ (lower:upper bound)-$T_{\text{columnar-isotropic}}$ (lower:upper bound) of most polymers in the range.

[**] Some uncertainty about true absence of longitudinal positional long range order in the lower part of temperature range.

Polymers that exhibit the hexagonal columnar phase but contain no discotic, phasmidic or other conventional columnar mesogens are listed in Table 1 [27].

Table 1 is divided in three sections. Section A lists the strictly main-chain polymers while section B lists polymers with relatively small sidegroups which are, most often, single *n*-alkyl chains. Macromolecules with more than one flexible tail in the sidegroup are excluded as these could be regarded as more conventional columnar mesogens. The backbones in group B polymers are flexible. In contrast, polymers in section C have rigid backbones and they or their equivalents also form lyotropic phases.

Polymers in section B all have inorganic backbones, and it can be argued that the reason that they form columnar liquid crystals may be somehow related to the tendency for microphase separation. However, interesting insight into this type of mesophase has been provided by the finding by Papkov and coworkers [45] that polyphosphazenes with butoxy and pentoxy sidegroups display a re-entrant isotropic phase. Thus e.g. for the pentoxy polymer (PDAP-C5) the sharp 10 diffraction peak of the $\mathrm{Col_h}$ phase broadens on cooling to room temperature and below. This in itself would not be unusual, since such behaviour is observed in most columnar and cubic phases when the glass transition is reached. However in PDAP-C5 $T_g \cong -90°\mathrm{C}$. More significantly, thermomechanical measurements revealed that the phase between T_g and room temperature is a soft rubber, with the modulus increasing substantially on heating to the $\mathrm{Col_h}$ phase – see Figure 8a–d.

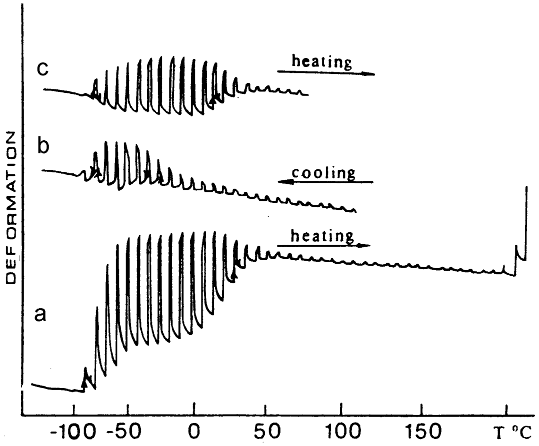


FIGURE 8 Differential thermomechanical traces of poly(di-*n*-pentylphosphazene): (a) first heating scan, (b) cooling scan, (c) second heating scan. The sample is periodically loaded and unloaded in compression. Heating/cooling rate is 5°C/min. The approximate transition temperatures are: glass $\xrightarrow{-90°\text{C}}$ re-entrant isotropic (rubber) $\xrightarrow{r.t.}$ Col_h $\xrightarrow{200°\text{C}}$ isotropic/degradation (after [45]).

The interpretation of the above anomaly is by no means certain, and a theoretical study is currently underway [56]. One possibility is that, because of the long –P=N–P– distance, alkoxy chains attached to successive phosphorus atoms are too far apart to fill space while in the all-*trans* conformation. Thus at low temperatures, with the side-chains predominantly all-*trans*, the chain collapses to a random coil. At higher temperatures, as the side-chains become conformationally disordered and increase their effective cross-section, the main chain is stiffened, its persistence length increases and the columnar phase results. This qualitative picture is consistent with the stability of the Col_h phase above the range of the low-temperature isotropic phase. This interpretation could also account for the exceptionally high temperature stability of the Col_h phase in poly(dialkoxyphosphazenes) – isotropisation coincides with decomposition at 200°C. It may be that with increasing temperature coiling up of the backbone is countered by the laterally ever expanding side-chains, maintaining the stiffness of the chain. The anomalous behaviour of PDAP-C4 and PDAP-C5 may possibly explain the appearance of Col_h phase in all polymers in group B (Table 1). The flexible backbone is stiffened by conformationally disordered side-chains, the side-chain disorder, in turn, preventing interchain lock-in and the establishment of 3-d crystalline order.

In summary, while by no means comprehensive, this overview of the columnar phase in unconventional liquid crystal polymers demonstrates that columnar organization transcends the classical boundaries of what is commonly regarded as mesogenic material.

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