The Effect of Chemical Constitution on the Mesomorphic Behaviour of Tolan Polymers

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ABSTRACT. The development of the polymer structure, during the polymerization process, was found to play an important role in the formation of the liquid-crystalline structure. The polymer prepared from chiral $(+)-3-$methyladipoyl chloride displays a typical cholesteric mesophase texture. Liquid-crystalline properties and phase-transition temperatures were found to be affected less or more by the chemical constitution of the mesogens.

It is well known in low molecular weight liquid-crystalline molecules that even slight changes in the molecular structure (such as the geometry, polarity and polarizability), may cause surprising effect on their liquid-crystalline properties (Saeve 1979). The same phenomenon is found with thermotropic liquid-crystalline polymers. For examle, in liquid-crystalline main-chain polymers, the thermal stability of the liquid-crystalline phase diminishes with increasing flexibility of the polymers and thus parallels the behaviour of low molecular weight systems.

Thus, the polymer corresponding to structure (I) does not show liquid-crystalline behaviour.

$$-\left[-OC-\bigcirc-N=N-\bigcirc-C(O)O(CH_2)_n\ O-\right]_x-$$

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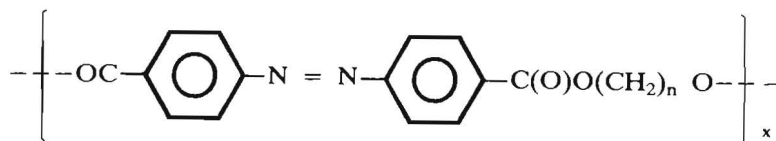
In sharp contrast, removal of the carbonyl group one atom away from the benzene ring (by exchanging the sequence of ether and carbonyl linkage) as in the polymer structure (II) produces very thermally stable liquid-crystalline polymers.

$$-\left[-O-\left\langle\bigcirc\right\rangle-N=N-\left\langle\bigcirc\right\rangle-OC(O)(CH_2)_n\ CO-\right]_x-$$
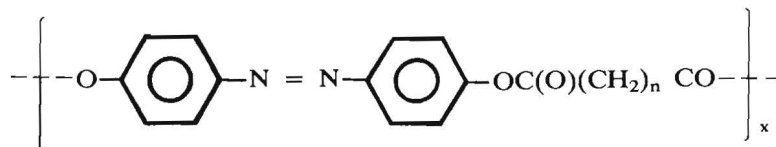
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Furthermore, with polymers the polymerization process itself can lead either to a diminution in the liquid-crystalline properties compared to the mesogen or to the introduction of a certain degree of order to form a stable mesophase. to test these concepts, we have synthesised a variety of polymers, mainly derived from the tolan unit which, in conjunction with suitable spacers, form, stable mesophase homopolymers (Tn) and copolymers (Al-Dujaili *et al.* 1985, 1988).

$$-\left[-O-\left\langle\bigcirc\right\rangle-C=C-\left\langle\bigcirc\right\rangle-OC(O)(CH_2)_n\ CO-\right]_x-$$
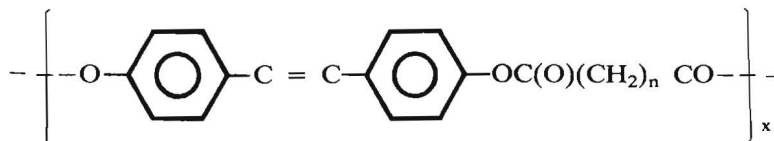
$-Tn-$

Experimental

Preparation of monomers

P,P'-dihydroxy tolan ($HOC_6H_4\ C\equiv CC_6H_4\ OH$) and P,P'-dihydroxy tolan diacetate have been prepared according to a procedure described earlier (Al-Dujaili *et al.* 1985), P,P'-tolan diacrylate was synthesised as described in the reference (Strzelecki *et al.* 1973). It has transition temperatures of C 135 N 145 I.

Poly (β-aminoester) containing tolan diacrylate unit

$$[-CH_2\ CH_2C(O)OC_6H_4C\equiv CC_6H_4\ OC(O)CH_2\ CH_2-N\left\langle\bigcirc\right\rangle N-]_x$$
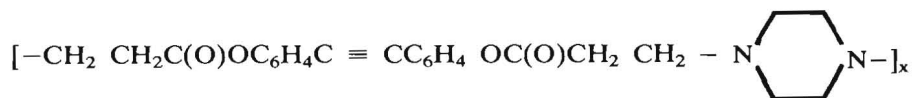
Under a stream of dry N_2, a solution of anhydrous piperazine (0.22g, 2.5 mmol) (Aldrich) in dry 1,4-dioxane (10cm^3) was added dropwise to a solution of P,P'-tolan diacrylate (0.8g, 2.5 mmol) in the same solvent (10cm^3). The mixture was stirred for 24h at rooom temperature and then poured into a large excess of aceton. The polymer formed as a yellow powder was washed by aceton, H_2O and then dried in vacuum. Found: C, 70.9; H, 6.0; N, 6.8; $C_{24} H_{24} O_4 N_2$ Cale.: C, 71.3; H, 5.9; N, 6.9.

P,P'-dihydroxy-1,3-bis (P-phenoxymethyl) tetramethyl disiloxane was synthesised in three steps, as described in reference (Jo *et al.* 1982).

Preparation and characterization of polymers

The monomers were prepared with the tolan component, using the general polymerization procedure described earlier (Al-Dujaili *et al.* 1985).

Inherent viscosities were determined at 30°C using a solution of polymer (0.5g) in a 60/40 mixture of phenol and tetrachloroethane (100 cm^3). A viscomatic MS-type 5300 Fica viscometer was used.

Thermal behaviour was determined with a Perkin-Elmer DSC-2 instrument. All the runs made under a nitrogen atmosphere with a heating or cooling rate of 20 K/min. The maximum temperature of the endotherm was taken as the transition temperature. The calculated values of $\triangle H$ were based on the endothermic peak areas in the thermogram and on the weight of the sample used, based on indium ($\triangle H_m = 6.8$ cal g^{-1}) as a standard.

The optical observations were made on a Leitz polarizing microscope Metler FP2 equipped with heating stage and photographic camera. Polymer texture was studied between a slide and cover slip, using slight pressure at the phase transition temperature. Nitrogen gas was passed over the sample during the course of the observations.

Results and Discussion

Effect of Flexibility

As mentioned earlier, a change of the flexible spacer was accompanied by a considerable change in liquid-crystalline properties. Recently, highly flexible siloxane segments have been reported to yield glassy mesomorphic polymers with liquid-crystalline properties extending over an exceptionally wide range of

temperature, *i.e.* over 300°C, between the glass transition temperature (t_g) and the isotropic temperature (t_i) (Agullera *et al.* 1983). Tolan polymers (Al-Dujaili *et al.* 1988) are to some extent thermally stable (especially with moderately flexible spacers) but the isotropization temperature is very high. Thus, the insertion of flexible siloxane spacers into the backbone of the tolan polymers might be expected to enable us to produce liquid-crystalline polymers with lower isotropization temperatures. We have synthesised a polymer containing 50% P,P'-dihydroxy tolan and 50% P,P'-dihydroxy 1.3-bis(phenoxymethyl)tetramethyldisiloxane with sebacyl chloride.

The thermal properties of this polymer (designated as CTSi/8), as determined by DSC, in addition to these of T8, are presented in Table 1 (T8 data were taken from reference (Al-Dujaili *et al.* 1985). As expected, the flexible dimethylsiloxane spacers exercise a remarkable influence on t_{lc}. The replacement of 50% of the tolan units by siloxane units leads to a decrease of 86°C in the melting temperature. Another point of interest is the fact that the $\triangle H_{lc}$ of CTSi/8 is much lower than that for the polymer T8. Apparently, this can be attributed to the effect of siloxane flexibility, irregularity, and to its steric bulkiness, all of which would be expected greatly to reduce either or both the interchain interaction and the degree of the crystallinity of the polymer. Normally, the longer flexible spacers introduce a high degree of molecular order into the polymer chain, probably due to the dilution effect. In the polysiloxane, more structural order would be expected, because, according to Jon and Robert (Jon and Robert 1969), the methyl groups in poly(dimethylsiloxane) rotate with unusual ease around the Si-O bonds, even at as low a temperature as −195°C. Thus, one might expected that the isotropization entropy for CTSi/8 should be larger than that for T8. However, such an ordering is accompanied by a narrowing of the liquid-crystalline temperature range of the polymer, $\triangle S_i$ benig unavaliable due to decomposition of CTSi/8 in DSC scan.

The CTSi/8 texture appears on the hot stage of the polarizing microscope with large extinction bands (Fig 1). By increasing the temperature of the hot stage, these

Table 1. Properties of copolymer CTSi/8

Polymer Designation	η_{inh} dL/g	t_{lc} °C	$\triangle H_{lc}$ Kcal/mol^{-1}	t_i °C	$\triangle S_i$ cal / mol^{-1}K^{-1}
CTSi/8	0.35	161	0.55	a	–
T8	0.20	247	1.08	350	0.96

(a) Signifies that the transition is obscured by decomposition.
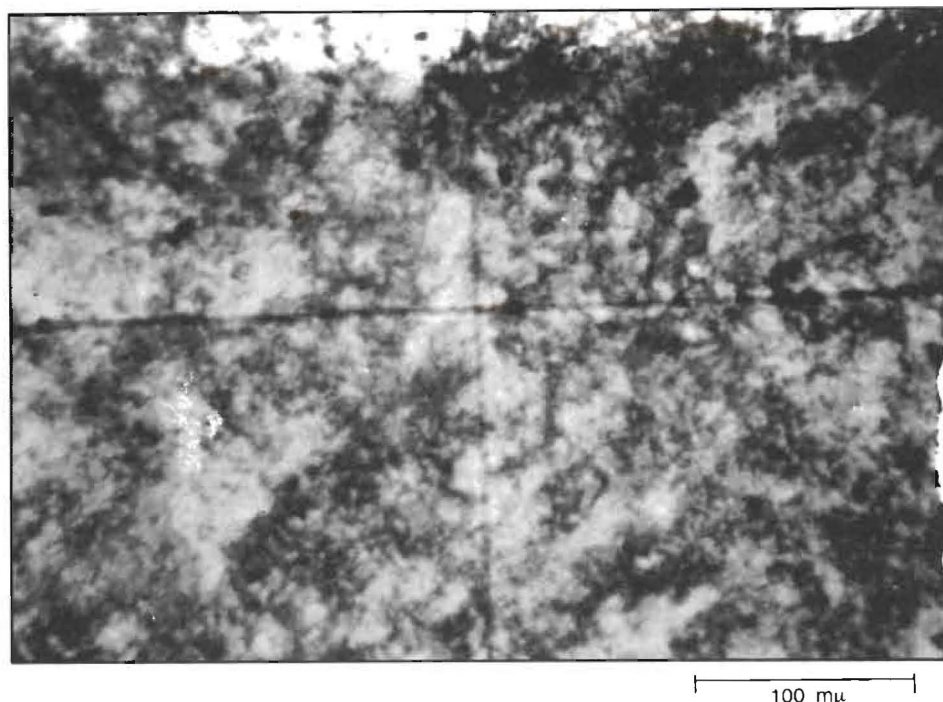
100 mµ

Fig. 1. Extinction band texture of CTSi/8 at room temperature (between crossed polars).

bands become progressevely larger with the appearance of some homeotropic islands. The homeotropic region appears black when viewed between crossed polars because the molecular axis is aligned in the same direction as the incident light beam. At 160°C, the polymer changes completely to the homeotropic state; on cooling it returns to a very similar extinction-band texture.

Effect of polymerization

As is well known, the main-chain thermotropic polymers can be obtained either by incorporating a mesogenic group (which has a tendency to form liquid-crystalline phases) in the polymer backbone, or by incorporating nonmesogenic groups which nevertheless result in a polymer system which shows liquid-crystalline properties due to the introduction of order during the development of macromolecular structure through polymerization. It is apparent, from our observations reported in this section, that mesomorphic properties of the polymer depend, to a certain extent, on the macromolecular structure produced during the polymerization process and not only on the mesogenic unit which is incorporated in the main-chain.

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The monmer p,p'-tolan diacrylate exhibits two endotherms on heating in the DSC, one at 135°C and the other 145°C. Observations with the polarizing microscope at 139°C indicate that this compound shows a nematic texture with defects typically in the form of dark threads (Fig. 2). When the nematic phase is slowly heated to 144°C, a round droplet having extinction lines appears (see Fig. 2b), some degradation occuring at the clearing point (Fig. 2b, right-hand side).
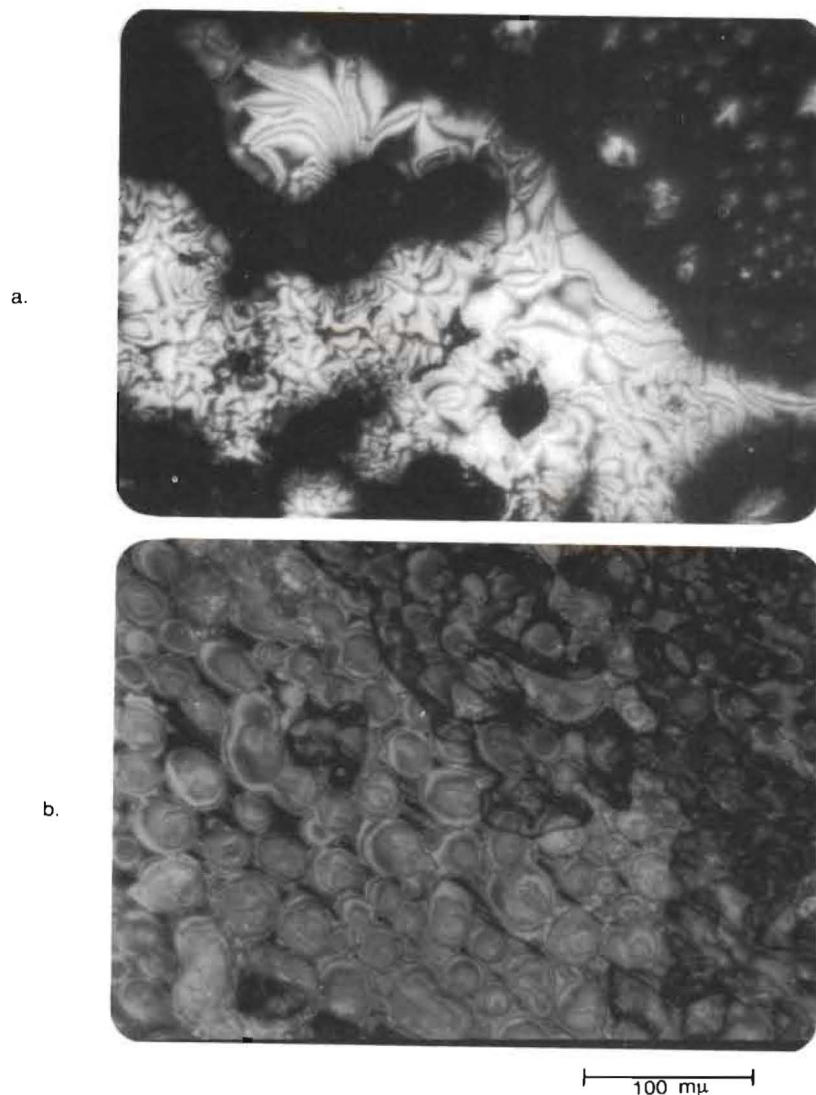
a.

b.

|⎯⎯⎯⎯⎯⎯⎯⎯⎯|
   100 mµ

Fig. 2. Photomicrographs viewed between crossed polars of P,P'-tolan diacrylate
a) Nematic texture at 130°C.   b) Nematic droplet having extinction bands.

Poly (β-aminoester) (see the experimental) does not show any liquid-crystalline behaviour but simply changes from the solid state to the isotropic fluid at 240°C. This polymer has considerable structural similarity to T6, but the linearity in the former polymer depends upon wheather or not the piperazine units in the plane of the polymer repeating unit. The piperazine unit will, however, in this case allow thermal vibration to cause the polymer to adopt a kinked non-linear arrangement as a result of flexibility introduced by the piperazine bridge.

An analogous case was found with the non-mesogenic tolan compound (III) (Verbit and Tiggey 1972).

$$RO-\langle O \rangle-CH_2OC(O)C \equiv CC(O)OCH_2-\langle O \rangle-OR$$

–**III**–
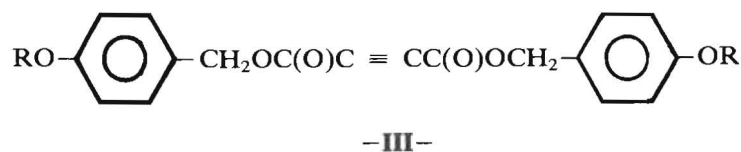
whereas the corresponding (IV) derivative is mesogenic.

$$RO-\langle O \rangle-OC(O)C \equiv CC(O)O-\langle O \rangle-OR$$

–**IV**–
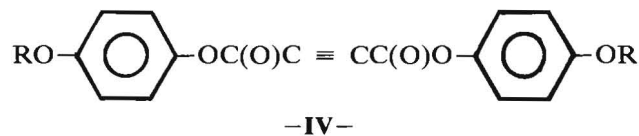
In general, the introduction of methyl groups near the rings (benzene or, in poly (β-aminoester) , piperazine) may cause significant deviation from linearity leading to a decrease in mesophase stability.

Another interesting point is that Malthete *et al.* reported (Malthete *et al.* 1973) that the tolan derivative of structural formula (V) is not mesomorphic but forms an isotropic liquid at 111°C.

$$Me(CH_2)_4\ C(O)O-\langle O \rangle-C \equiv C-\langle O \rangle-OC(O)(CH_2)_4Me$$

–**V**–
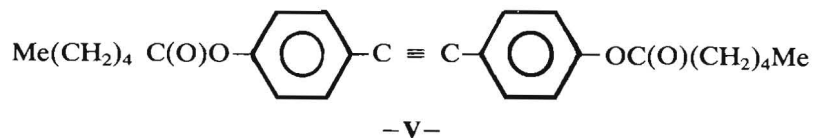
This molecule (V) represents the model compound for the tolan polymer T4, which exhibits liquid-crystalline properties, as we have shown in a previous

publication (Al-Dujaili *et al.* 1985). Thus, here we have the inverse of the previous phenomenon, that is, on polymerization of non-mesogenic units a mesogenic polymer can be formed, the increase in order being a direct function of the polymerization process.

Cholesteric polymer

Studies on low molecular weight liquid-crystalline molecules shown that a nematic structure can be transformed to a cholesteric helical structure by incorporation of a chiral centre, either by chemical reaction or in physical admixture. Thus, copolymerization of a nematogenic monomer, exhibiting a nematic phase as a homopolymer, with chiral monomer should result in an induced cholesteric phase polymer. Finkelmann *et al.* (Finkelmann *et al.* 1978) described the synthesis of the first side-chain thermotropic cholesteric polymers. Blumstein *et al.* (Blumstein *et. al.* 1982) have also used this idea, and prepared a homopolymer and copolymer exhibiting cholesteric mesophase. This type of structure may have considerable techonological interest (Ciferri *et al.* 1982).

We have prepared a cholesteric polymer by reacting the P,P'-dihydroxytolan with a chiral compound (+)-3-methyladipyl chloride yielding a polymer of structural formula VI.

$$\left[O-\bigcirc-C\equiv C-\bigcirc-OC(O)CH_2CH_2CH(CH_3)CH_2CO \right]_x$$

$$-VI-$$
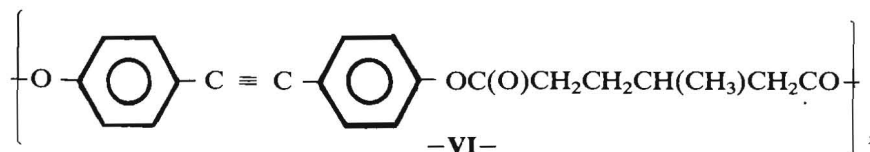
This polymer is designated T_{ch} and as expected, shows a cholesteric mesophase. The thermal properties along with the η_{inh} of the polymer are given in Table 2. Fig. 3 shows that the introduction of asymmetric centre in a polymer backbone causes formation of the typical texture of planar cholesteric, that is, with oily streaks.

Table 2. Properties of T_{ch} polymer

Polymer Designation	η_{inh} dL/g	t_{lc} °C	$\triangle H_{lc}$ Kcal/mol^{-1}	t_l °C
T_{ch}	0.38	281	0.51	a

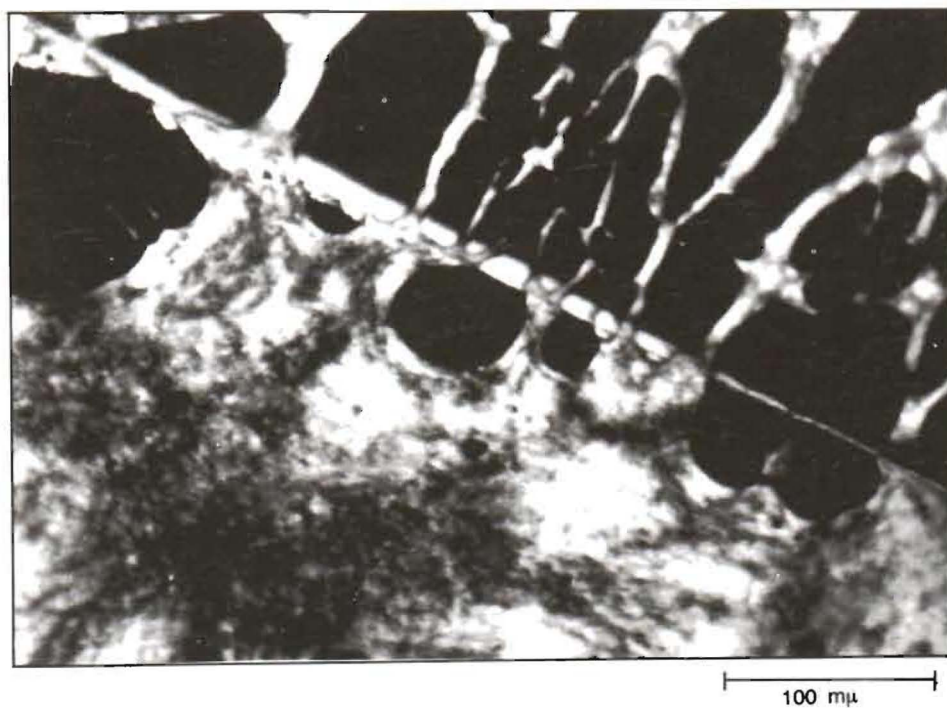(a) Has the same meaning as in table 1.

100 mµ

Fig. 3. Photomicrographs of quenched cholesteric mesophase of polymer T_{ch} with, "oily streaks" (between crossed polars).

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تأثير التراكيب الكيميائية على الخواص البلورية السائلة لبوليمرات التولان

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حضرت سلسلة من البوليمرات التي تحتوي على جزيئة بارا ـ بارا ثنائي هيدروكسي التولان في هيكلها الجزيئي ، اظهر عدد من أفراد هذه السلسلة خواصاً بلورية سائلة بينما لم يظهر هذه الخواص البعض الآخر منها . وقد تحقق من وجود الخواص البلورية السائلة باستخدام مسعر المسح التفاضلي (DSC) ، قياس عدد اللزوجة اللوغاريتمية (η inh) والمجهر المستقطب المزود بمسخن ، لقد تبين أن التركيب الجزيئي للبوليمرات خلال عملية البلمرة يلعب دوراً مهماً في إظهار الخواص البلورية السائلة .

ان عملية البلمرة لمونمرات ليست لها القابلية على إظهار الخواص البلورية السائلة قد تؤدي إلى تكوين بوليمرات تمتلك هذه الخواص بالاعتماد على الانتظامية التي تحصل خلال عملية البلمرة . وبالعكس قد تمتلك مونمرات خواصاً بلورية سائلة تفقدها خلال عملية البلمرة لفقدان الانتظامية والخطية الواجب توفرهما في التركيب الجزيئي للبوليمرات البلورية السائلة .

ان إدخال سلاسل مرنة تحوى ذرات السيليكون في داخلها في الهيكل الرئيس للبوليمرات البلورية السائلة يؤدي إلى إنخفاض درجات الانصهار لهذه البوليمرات مما يسهل عملية دراستها في درجات الحرارة هذه دون خضوعها لعملية التأكسد أو التحطم . ان حرية حركة مجاميع المثيل المعوضة على ذرات السيليكون هي المسؤولة عن إنخفاض درجات الانصهار .