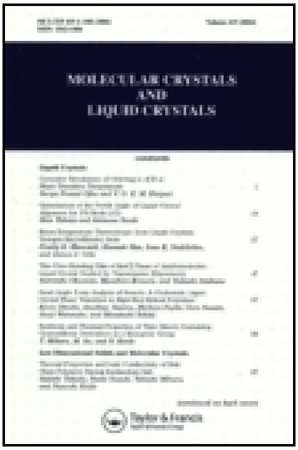

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Mesophase Formation in Polymers With Anisometric Side-Groups in Relation to Their Chemical and Stereochemical Structure†‡

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The influence of the flexibility of the polymer main chain on the smectic ordering has been investigated, by means of optical, diffractometric and calorimetric techniques, in several polymers carrying rigid anisometric side-groups. The effect of the chemical structure of the side-groups has been examined throughout: atactic polymers with biphenylyl side-groups may be amorphous or mesomorphous depending on the nature of the groups linking the biphenylyl moiety to the backbone chain. Correlations between the molecular weight and the stereochemical structure of the macromolecules and the occurrence of a thermotropic smectic phase in a series of polyacrylates and polymethacrylates, have been reported.

INTRODUCTION

Mesomorphic polymers form a new class of polymers characterized by a structural order very similar to that of liquid crystals. In the past few years polymers containing anisometric side groups and displaying smectic, nematic and cholesteric mesophases have been synthesized, and their general properties described. The major difference between these macromolecular compounds and liquid crystals lies in the physical state of the mesophases. In fact, whereas liquid crystals display ordered phases in the fluid state, most polymer mesophases give rise to solid and rigid structures. This is not surprising, since

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in polymers the groups which have a tendency to form liquid-crystalline phases are bonded to a backbone chain, so that the translational motions of these groups are prevented while the main chain maintains its conformational rigidity. The same effect is obtained if smectics, nematics or cholesterics are reticulated. As shown by Strzelecki *et al.*,[1] the reticulation process, which takes place in an isotropic fashion, results in a "solid liquid-crystal" the bulk optical properties of which are identical to those of the original liquid crystal. However, polymer mesophases do not necessarily have to be obtained by polymerization of monomers in their liquid-crystalline state: we first demonstrated[2] that polymers characterized by a thermodynamically stable mesophase can be obtained by polymerization of non-mesogenic monomers. Clearly the structure of the repeating unit is very important in determining whether or not a polymer can display thermotropic mesophases.

In this paper we will report on studies carried out in this laboratory aimed at elucidating the influence of the molecular structure on the degree of order and transitions occurring in mesomorphic polymers with anisometric side groups.

EXPERIMENTAL

Materials

Atactic polymers were prepared by radical polymerization in bulk or in solution, using Bz_2O_2 as initiator. In most cases, the parent monomers were not mesomorphous.

Isotactic PPBA (poly(*p*-biphenylyl aerylate)) was prepared by polymerizing the monomer in toluene at −78°C with BuLi as initiator. Fractionation with appropriate solvents led to a sample with a degree of isotacticity higher than 97%.

Isotactic and syndiotactic PPBMA were obtained by polymerization with BuLi as initiator at −78°C in toluene and THF respectively. The degrees of tacticity for the different PPBMA stereoisomers were: isotactic sample: $i = 90\%$; radical polymerized sample: $s = 80\%$; syndiotactic sample: $s = 90\%$.

Techniques

Polymer molecular weights were determined with the usual osmometric and GPC techniques.

X-ray diffraction data were obtained using a Norelco wide-angle diffractometer with CuKα radiation.

Optical measurements (T.O.A.) were made with a polarizing microscope attached to a programable heating stage (Mettler FP5 and FP52) and to a photometer and recorder.

Calorimetric measurements were made with Perkin Elmer DSC–1b and DSC–2 apparatus.

The dynamic elastic modulus was determined using a resonance electrostatic apparatus at frequencies of 10^3–10^4 Hz, with specimens in the form of disks of 36 mm diameter and 2 mm thickness.

Tensile data were obtained with a CS–183 Tensile Tester (by C.S.I.) equipped with a thermostatically controlled air chamber. Specimen temperature was monitored with a digital thermometer. Tests were performed at a straining rate of 0.125 in min^{-1}. Specimens were moulded with a CS–183 Molder (by C.S.I.) at 280°C. A specimen gauge section was about 1.6 mm in diameter and about 9 mm long.

RESULTS AND DISCUSSION

In principle, the mesomorphic polymers containing anisometric side groups which have a tendency to form liquid crystalline structures can be divided into two main categories:

A) polymers containing mesogenic groups in the side-chains, decoupled from the backbone chain by flexible groups ("spacers")

B) polymers containing rigid anisometric side-groups directly bonded to the main chain.

In both cases, if the intermolecular attraction between active groups is strong enough and the flexibility of the main chain (or of the spacers) provides for easy lateral fitting of these groups, a state of substantial order of the smectic type is achieved. The structures of these two different kinds of smectic polymers are schematically reported in Figure 1. In the first case, the dimension of the smectic layers d_1 is less than the lateral dimension d_3 of the macromolecule. In the second case, the dimension of the smectic layer corresponds to the lateral dimension of the macromolecule, since the interplanar spacing is approximately twice the length of the side groups.

In this respect it could be anticipated that some of the general properties of these two groups of polymers have to be different depending on the different way of packing of the smectic layers, and on the different distribution of the amorphous regions in the bulk polymer. It would be expected that differences in the layer structure affect the thermal and mechanical behaviour of these polymers especially above the glass transition temperature, T_g. In

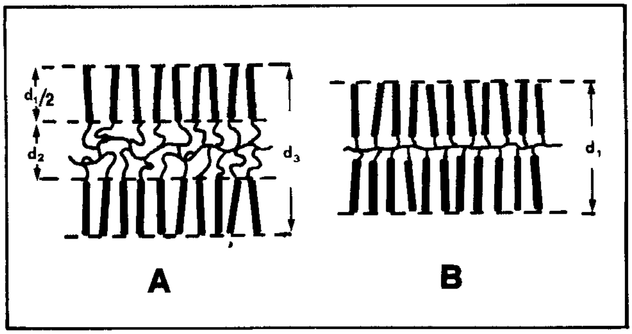
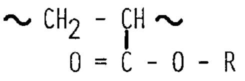
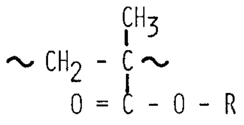


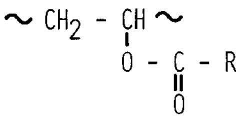
FIGURE 1 Shematic representation of the layer structure of smectic polymers with mesogenic groups in the side chains decoupled from the backbone chain by flexible spacers (A) and polymers with anisometric side-groups directly bonded to the main chain (B).

particular it has been found that the melting point or the temperature at which complete destruction of the organized structures occurs, is usually much higher in polymers where the rigid side-groups are directly bonded to the main chains than in polymers where the same groups are spaced from the polymer chain by flexible groups.

TABLE I


$$\begin{array}{l}\sim CH_2 - \underset{|}{CH} \sim \\ \quad\; O = C - O - R\end{array}$$


$$\begin{array}{l}\quad\quad\;\; \overset{CH_3}{|} \\ \sim CH_2 - \underset{|}{C} \sim \\ \quad\; O = C - O - R\end{array}$$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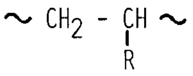
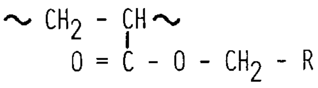
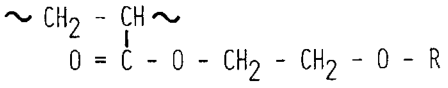

$$\begin{array}{l}\sim CH_2 - \underset{|}{CH} \sim \\ \quad\quad\quad\; R\end{array}$$


$$\begin{array}{l}\sim CH_2 - \underset{|}{CH} \sim \\ \quad\; O = C - O - CH_2 - R\end{array}$$


$$\begin{array}{l}\sim CH_2 - \underset{|}{CH} \sim \\ \quad\; O = C - O - CH_2 - CH_2 - O - R\end{array}$$

Actually we will concentrate on polymers belonging to class B, showing the effect of the nature of the main chain on the ordering ability and on the degree of order of these materials.

In Table I are reported polymers with different main chain structures, containing the biphenylyl moiety in the side-groups.

X-ray and calorimetric data demonstrated that in cases where the biphenylyl group is linked to polyvinyl, polyvinyl ester and polymethacrylic chains, the relevant polymers were amorphous. Only when the biphenylyl group is attached to a polyacrylic chain is a highly ordered material obtained —(poly(*p*-biphenylyl acrylate) (PPBA)).

The X-ray diffraction pattern of a powder sample of atactic PPBA, melted at 290°C and then slowly cooled to room temperature, is reported in Figure 2. It shows an intense, sharp reflection at $2\theta = 3.8°$ corresponding to a periodicity of 23.2 Å. Several high orders of this reflection are also visible. A wide-angle halo, typical of the amorphous material, indicates the absence of regular lateral periodicities in the packing of the side-groups. This diagram is consistent with a structural model in which the rigid side-groups are extended at right angles on both sides of the main chains and these are confined to planes spaced by ~23 Å. On the basis of these results a smectic A structure has been assigned to this polymer.

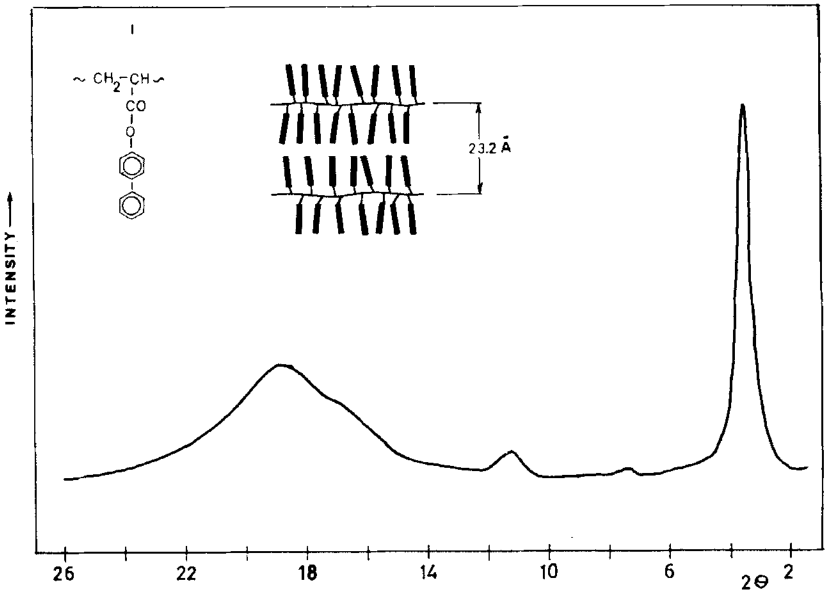


FIGURE 2 Powder X-ray diffraction pattern of atactic PPBA.

The occurrence in PPBA of a smectic mesophase is the result of a favourable combination of properties such as the polarity of the —CO—O— group, the orientation of the dipole carried by the acryloyloxy group to which the biphenylyl group is bonded, and the flexibility of the backbone chain. It should also be noted that the replacement of one phenyl ring by a cyclohexane ring does not change the smectic organization of the polymer.[3] These facts suggest that in these polymers the mesomorphic phase is brought about by a "lock and key" mechanism involving the polyacrylic chain and the biphenylyl or the *p*-cyclohexylphenyl groups. This is confirmed by the results obtained on the last two polymers in Table I. X-ray, calorimetric and optical observation showed that these polymers are amorphous and isotropic.[4] Thus, the introduction of short flexible groups between the main chain and the biphenylyl group is sufficient to suppress such interaction and the ordering of the side-groups is completely prevented.

As regards the effect of stereoregularity on the ability of these polymers to organize spontaneously into mesomorphic structures, two examples will be considered here: PPBA and poly(*p*-biphenylyl methacrylate) (PPBMA).

In the case of PPBA, samples of atactic and highly isotactic polymers of comparable molecular weight, were examined. Both polymers show the same X-ray pattern even after prolonged high temperature annealing. This is a significant result indicating that interaction forces between side-groups prevent the backbone of the isotactic polymer from assuming a helical conformation. The advantage of the extended chain conformation over the helical conformation of an isotactic polymer is the better spatial filling of the former and the closer packing of the side-groups. In this connection it should be noted that for the isotactic molecule to be able to assume such a conformation, it is most likely that rotations and distortions of the main chain occur that cause irregularities in the spatial arrangement of the backbone atoms. This may account for the absence of order along the polymer chain axis.

Although the stereoregularity does not appreciably change the state of order of PPBA, some remarkable differences in the thermal behaviour between atactic and isotactic polymers can be observed (Figure 3). This is probably due to differences in the details of the smectic structures of these two stereoisomers which cannot be revealed by X-ray analysis.

In the same way as the stereoregularity does not affect the smectic ordering of PPBA, it does not change the amorphous character of PPBMA. In this case, only a change of the glass transition temperature is observed. T_g is seen to increase in the order: isotactic, radical polymerized, syndiotactic PPBMA (Figure 4). These results are consistent with those reported for the stereoisomers of PMMA.[5]

We want to consider now the case of polymers containing rigid anisometric side-groups different from the biphenylyl group. In Table II are reported a

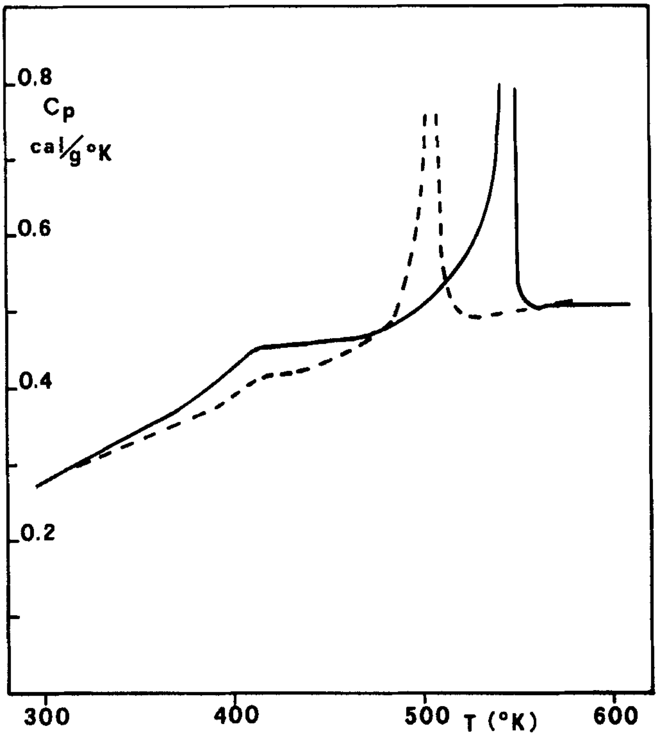


FIGURE 3 Specific heat capacity as a function of temperature for atactic (——) and isotactic (– – –) PPBA.

series of polyacrylates and the corresponding polymethacrylates carrying potential mesogenic side-groups of different structure.

In principle it would be expected that an enlargement of the side-groups, by increasing the number of stiff and highly polarizable units, would bring about a corresponding increase of the mesogenicity of such groups, so that they could become organized in spite of the hindering effect of the polymethacrylic chain. However, this has not been found for the polymers examined, as demonstrated by the X-ray analysis (Figure 5).

From a comparative analysis of the thermal behaviour of the different polyacrylates and polymethacrylates (Figure 6), one realizes that the behaviour of polymer 8 (*cf.* Table II) is somewhat anomalous. First of all, although X-ray analysis does not reveal the presence of ordered structures, this polymer exhibits a weak endotherm at about 290°C, which has to be related to a first order transition involving the existence of a mesomorphic phase. However, apart from any consideration of the degree of order that may exist, it should be noted that the overall behaviour of this polymer is different from that of all the other polymers examined. In Figure 7 and 8, comparative plots of the dynamic elastic modulus and birefringence as a

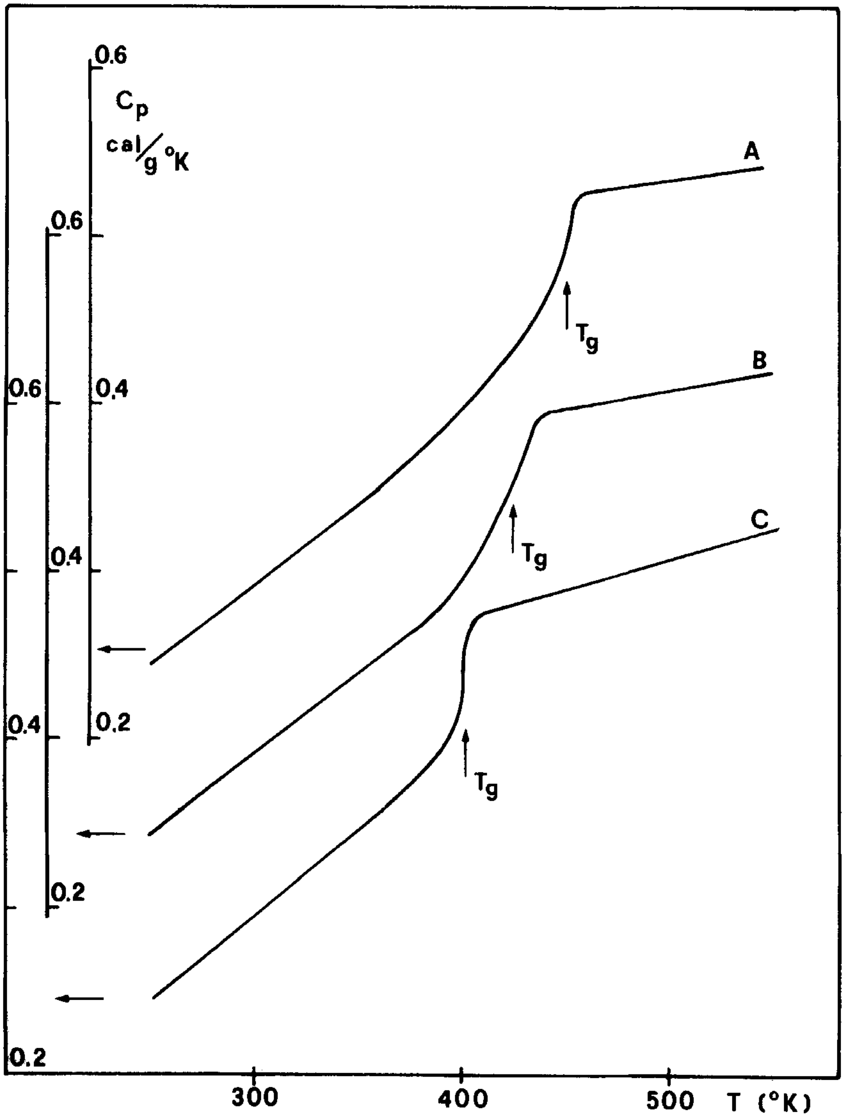
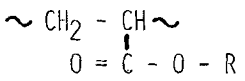
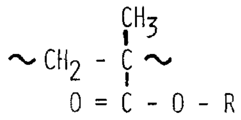


FIGURE 4 Specific heat capacity as a function of temperature for isotactic (C), radical polymerized (B), and syndiotactic (A) PPBMA samples.

TABLE II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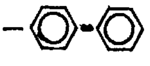
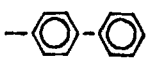
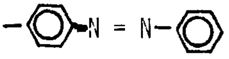
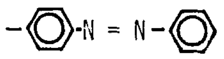
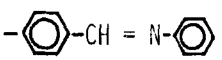
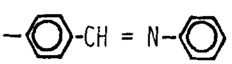
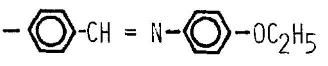
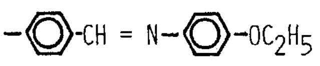
 1	 2
 3	 4
 5	 6
 7	 8

TABLE III

Properties of PPBA fractions with varying molecular weight

Fraction	$\bar{M}_n \times 10^{-3}$	$\bar{M}_n/\bar{M}_n$	$\|\eta\|$	T_m(°K)	$\Delta H_m(J/g)$
I (soluble in cold (C_6H_6)	12.5	2.9	0.07	508	9.0
II (soluble in boiling C_6H_6)	24.8	4.4	0.46	533	18.1
III (insoluble in boiling C_6H_6)	91.2	4.9	0.72	544	24.4

function of the temperature are reported together with the D.S.C. traces for polymer 8 and the corresponding polyacrylate (polymer 7, *cf.* Table II).

This latter, like all polyacrylates displaying a smectic mesophase, shows a distinct stepwise change in specific heat capacity at T_g ($\sim 100°C$). At this temperature a drop in the modulus *vs.* temperature curve of about one decade is observed. At the same temperature birefringent structures start to appear, and the birefringence steadily increases until the melting point of the polymer is approached. Above this temperature the birefringence rapidly decreases.

The non-zero birefringence which remains at temperatures above T_m is due to some crosslinking effect.

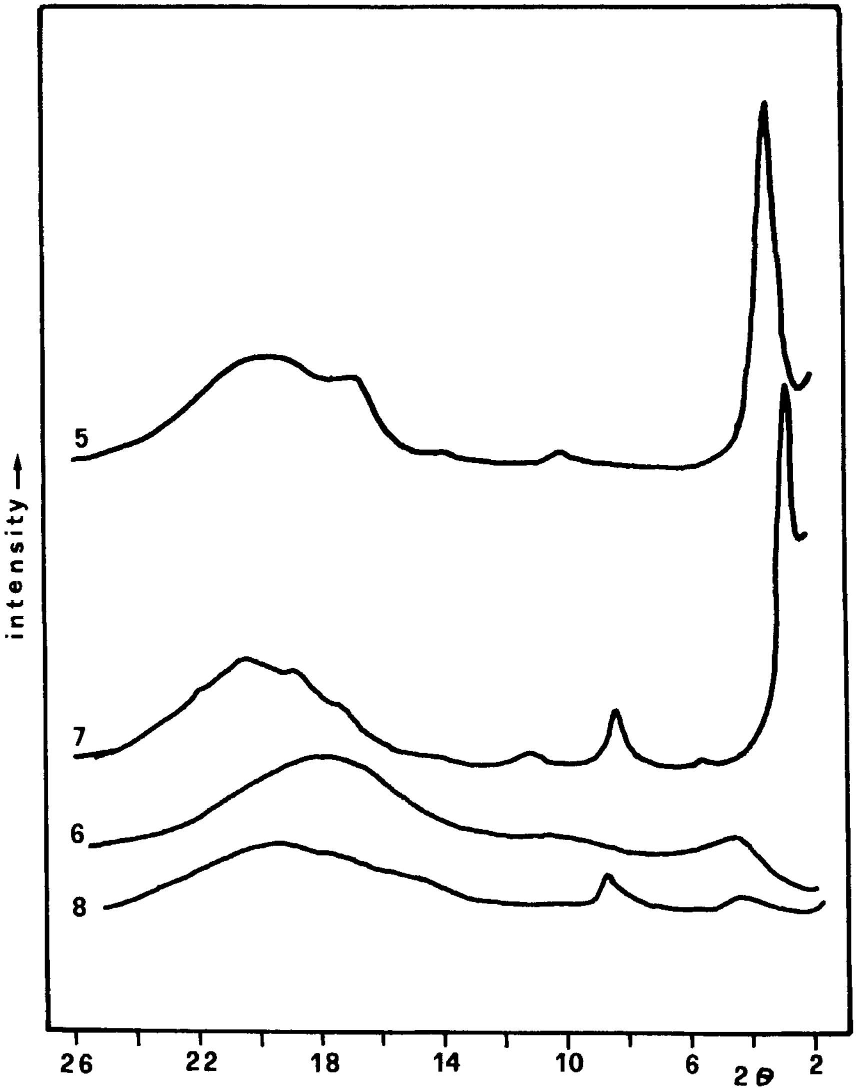


FIGURE 5 X-ray diffraction pattern of annealed samples of polyacrylates and polymethacrylates with rigid anisometric side-groups (*cf.* Table II).

For the corresponding polymethacrylate, a stepwise change of the specific heat is observed at about 200°C, which is assumed to correspond to the glass transition of the polymer. However, although the modulus drops to zero in the vicinity of this temperature (as normally observed for amorphous polymers), a very strong decrease of the modulus (almost one decade) occurs at considerably lower temperatures (about 80°C). On heating, birefringent structures are formed at this temperature and the birefringence increases until T_g is reached. Above T_g the birefringence decreases and in the proximity of the temperature corresponding to the endothermic peak in the D.S.C. traces (290°C), a zero birefringence is obtained.

This strange behaviour cannot be explained simply by admitting a low degree of smectic ordering in the bulk. Rather, the existence of structures less organized than smectic can probably account better for the anomalous behaviour of this polymer. On the other hand, structures of intermediate organization have been reported[6] for some polymers with similar molecular structure.

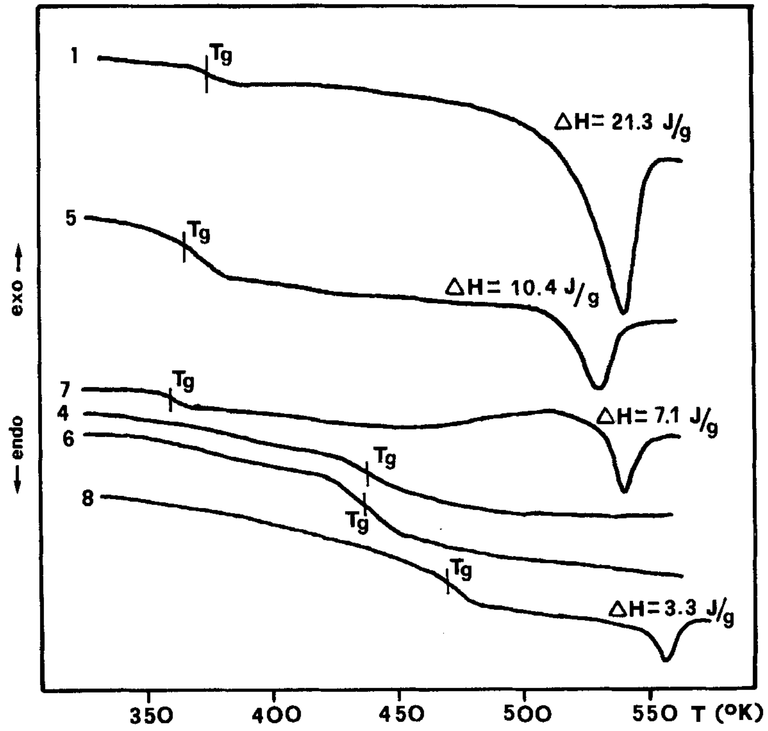


FIGURE 6 D.S.C. traces for annealed samples of polyacrylates and polymethacrylates with rigid anisometric side-groups (*cf.* Table II).

Finally, we want to illustrate the effect of molecular weight on the general properties of smectic polymers. It should be pointed out that, in view of the unusually large lateral dimension of these macromolecules (characterized by repeating units with long and bulky side-groups), it is more appropriate to refer to the average degree of polymerization rather than to the molecular weight in order to describe adequately the size and the shape of the macromolecules.

For PBBA it has been found that the degree of order increases on increasing the degree of polymerization. In other words, the value of the head-to-head distance of the macromolecules seems to be relevant for the attainment of a

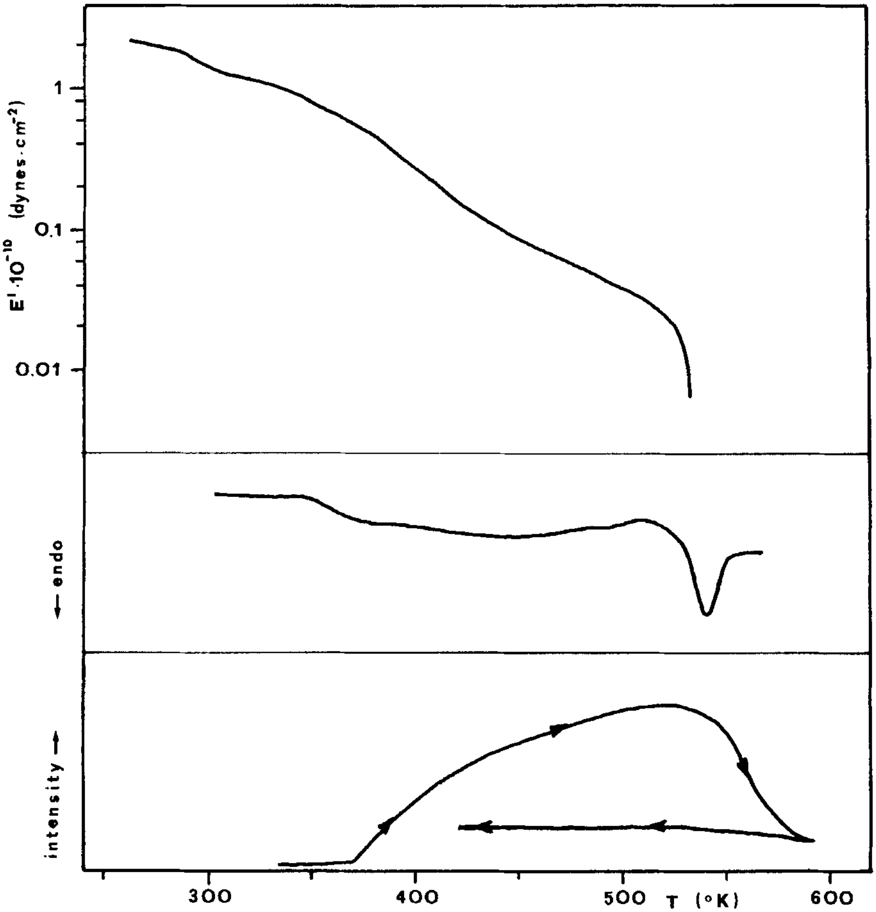


FIGURE 7 D.S.C. trace and temperature dependence of the dynamic elastic modulus and birefringence for polymer 7 (*cf.* Table II).

highly organized layered structure. This is demonstrated by the noticeable increase in the melting temperature T_m, and in the enthalpy of fusion ΔH, with increasing molecular weight (Table III).

The effect of the degree of polymerization on the mechanical properties of the polymer is still more striking. Clearly, the average linear dimension of the macromolecule is a factor of paramount importance for the attainment of good mechanical strength. In Figure 9 are reported the stress-strain curves obtained at different temperatures for samples of PPBA of high molecular weight. The polymer behaves as a brittle material at temperatures below T_g. Just above T_g there is a rather sharp brittle-ductile transition. At temperatures

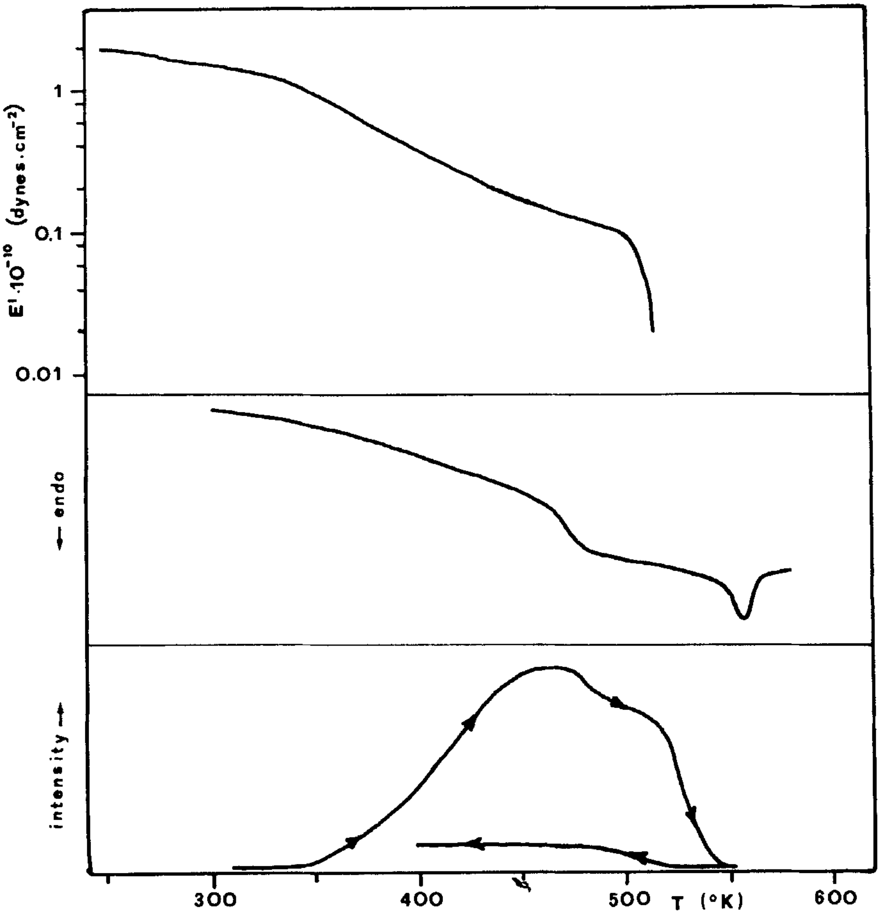


FIGURE 8 D.S.C. trace and temperature dependence of the dynamic elastic modulus and birefringence for polymer 8 (*cf.* Table II).

between T_g (110°C) and T_m (270°C) the material exhibits plastic deformation (necking), with values of the elongation required for breaking of the order of 100%. Above T_g the ultimate mechanical properties of PPBA are thus similar to those of many crystallizable polymers, with a rather high degree of crystallinity. For instance, the mechanical strength of PPBA is, at high temperatures, comparable with that of isotactic polystyrene of similar molecular weight, but, unlike isotactic polystyrene, PPBA exhibits a high elongation before breaking. This may be due to the particular layered structure of smectic polymers which allows large permanent deformation above the softening point of the amorphous regions.

It is interesting to note that a sample of PPBA stretched at about 200°C (sample obtained by cutting the portion of the test specimen where necking had occurred) shows a different shape of the endotherm corresponding to the melting process. The enthalpy of fusion is increased by about 20%, and also the melting temperature is increased by about 10°C (Figure 10).

These results can be explained if one admits that in the unoriented sample, the ordered domains do not extend uniformly throughout the specimen, the domains being interconnected by amorphous regions and/or regions where distortions of the smectic organization occur. Only by stretching the polymer above T_g can a high orientational order on a macroscopic scale be achieved.

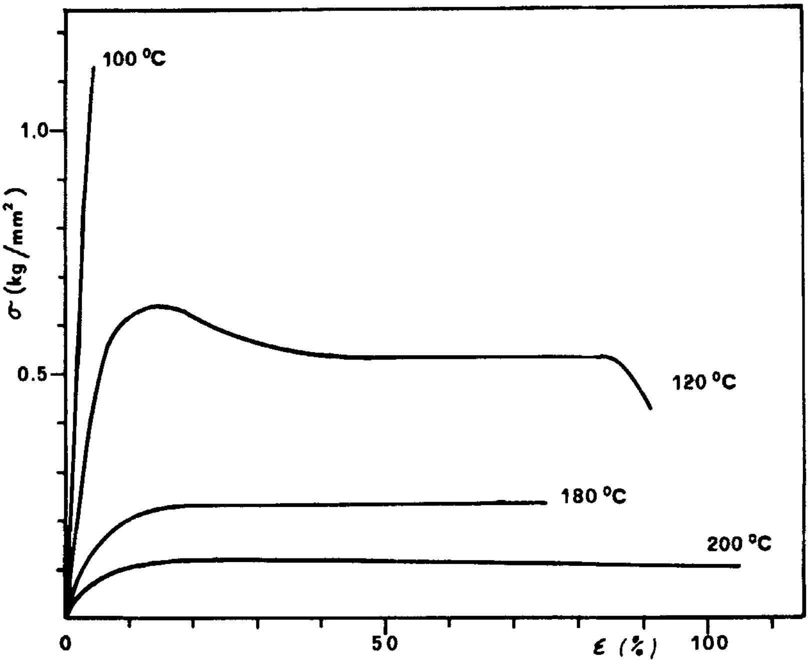


FIGURE 9 Stress-strain curves for smectic PPBA at different temperatures.

CONCLUSIONS

The results described outline some important features of mesomorphic polymers, especially of those obtained by polymerization of monomers containing rigid side-groups.

The results demonstrate that the nature of the main chain is very important in determining whether or not a polymer can display thermotropic mesophases. This is understandable since, in these polymers, the rigid side groups, which have a tendency to form mesophases in the bulk, are bonded directly to the backbone chain, so that it is the entire macromolecule which becomes mesomorphous.

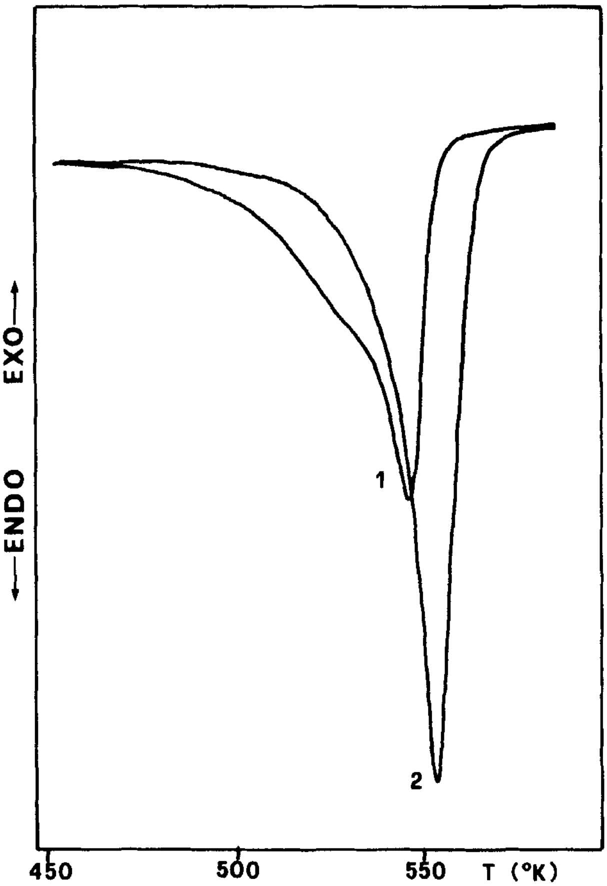


FIGURE 10 D.S.C. traces for unoriented (1) and oriented (2) smectic PPBA samples.

The results indicate also that the polyacrylic chain, more than others, facilitates the attainment of a smectic-like organization in macromolecular compounds.

It has also been demonstrated that, in cases where such a molecular organization exists, the ordering does not depend on the steric regularity of the backbone chain. This confirms that interaction forces between side-groups is the dominant effect in these macromolecules; the main chains, irrespective of tacticity, taking up some conformation to optimize side group packing.

Finally, results are presented which prove that mesomorphic polymers, with a sufficiently high degree of polymerization, possess ultimate mechanical properties which approach those of semi-crystalline polymers.

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