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The influence of the polymer backbone flexibility on the phase transitions of side chain liquid crystal polymers containing 6-[4-(4-methoxy-β-methylstyryl)phenoxy]hexyl side groups

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SUMMARY

The influence of the polymer backbone flexibility on the phase transition temperatures of side chain liquid crystalline polymethacrylate, polyacrylate, polymethylsiloxane, and polyphosphazene containing 6-[4-(4-methoxy- β -methylstyryl)phenoxy]hexyl side groups is discussed. Flexible backbones enhance the decoupling of the motions of the side chain and main chain and therefore, increase the rate of side-chain crystallization. Subsequently, the kinetically controlled crystallization process may transform the thermodynamically controlled mesomorphic phases from enantiotropic into monotropic. However, the highest degree of order in the mesophase is exhibited by the polymers based on the most rigid polymer backbone.

INTRODUCTION

Since Finkelmann, Ringsdorf and Wendorff (1) have advanced the spacer concept to decouple the motion of the side groups from that of the polymer backbone, research on side chain liquid crystalline polymers has received considerable interest both from fundamental and applied points of view. This field has been repeatedly reviewed (2, 3), most recently in a comprehensive book (4). In the liquid crystalline phase, the flexible spacer provides a partial decoupling of these two motions, which increases with the spacer length (5-7). It has been theoretically predicted (8) that the statistical random-coil conformation of the side chain liquid crystalline polymer becomes distorted and anisotropic on going from the isotropic to the liquid crystalline phase. This has been experimentally demonstrated for both nematic and smectic polymers (2, 6, 9). Based on these predictions and results, it has been recently suggested that for the same spacer length and mesogenic side group, the nature of the polymer backbone should be very important in determining the degree of decoupling (5). This is because the random-coil conformation of a flexible backbone is more easily distorted than that of a more rigid polymer backbone.

The goal of this paper is to describe the influence of four different polymer backbones which exhibit highly different flexibilities, i.e., a polymethacrylate, a polyacrylate, a polymethylsiloxane and a polyphosphazene, on the phase transitions of the corresponding polymers containing 6-[4-(4-

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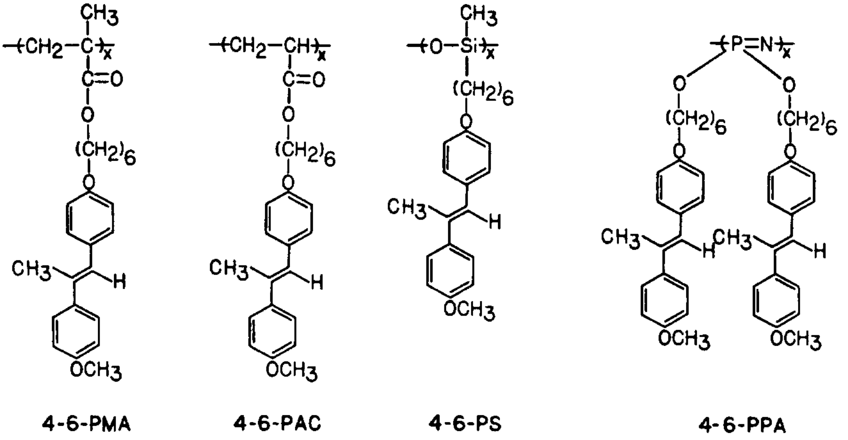
*To whom offprint requests should be sent methoxy- β -methylstyryl)phenoxy]hexyl side groups. Scheme 1 illustrates the structure of these polymers.



Scheme 1. The structures of polymethacrylate (4-6-PMA), polyacrylate (4-6-PAC), polymethylsiloxane (4-6-PS) and polyphosphazene (4-6-PPA) containing 6-[4-(4-methoxy- β -methylstyryl)phenoxy]hexyl side groups.

EXPERIMENTAL

Materials

6-[4-(4-Methoxy- β -methylstyryl)phenoxy]hexyl methacrylate (4-6-MA) and acrylate (4-6-AC) and their corresponding polymers (4-6-PMA and 4-6-PAC, respectively) were synthesized as previously described (10, 11). 5-[4-(4-Methoxy- β -methylstyryl)phenoxy]hexene and the corresponding polymethylsiloxane (4-6-PS) were synthesized as previously reported (10). The polyphosphazene (4-6-PPA) was synthesized by the nucleophilic displacement of the chlorine groups of a poly(dichlorophosphazene) with the sodium salt of [4-(4-methoxy- β -methylstyryl)phenoxy]hexan-6-ol as was previously described for the synthesis of other liquid crystalline polyphosphazenes (12). The synthesis of [4-(4-methoxy-β -methylstyryl)phenoxy]hexan-6-ol was reported previously (10). All polymers were purified by repeated precipitations from chloroform solutions into methanol until their analyses by GPC showed that they were free of starting monomers.

Techniques

The characterization of all polymers was performed by a combination of differential scanning calorimetry (DSC) (20°C/min), thermal optical polarized microscopy and gel permeation chromatography (GPC) according to standard procedures used in our laboratory (10, 13). Table I summarizes the molecular weights, the thermal transitions and the corresponding thermodynamic parameters of all polymers.

Table I. Characterization of polymers containing 6-[4-(4-methoxy-β-methylstyryl)phenoxy]hexyl side groups (g=glassy, k=crystalline, n=nematic, i=isotropic)

Polymer	$\bar{M}n\text{x}10^{-3}$	$\bar{M}w/\bar{M}n$	Phase Transitions (^{o}C) and Corresponding Enthalpy and Entropy Changes (ΔH in Kcal/mru / ΔS in cal/mru.^{o}K)	
	(GPC)		Heating	Cooling
4-6-PMA	40.5	1.9	g28n104(0.26/0.69)i	i 99(0.24/0.65) n20g
4-6-PAC[a]	3.3	1.2	g17k 91(2.07/5.69)i	i 90(0.11/0.30) n 6g
4-6-PAC	3.3	1.2	g10n 94(0.14/0.38)i	i 90(0.11/0.30) n 6g
4-6-PS	27.6	2.4	g-1k119(3.16/8.06)i	i89[b](0.04/0.11) n 65 (2.46/7.28) k-6g
4-6-PPA	2.3	1.9	g-2k124(2.61/6.57)i	i106(0.10/0.26) n 64 (1.57/4.66) k-7g

[a] first heating scan or after annealing the sample above T_g

[b] overlapped transitions

RESULTS AND DISCUSSION

The role of the polymer backbone, most commonly known as the "polymer effect", on the phase transitions displayed by a certain side chain liquid crystalline polymer, represents the result of a combination of thermodynamic and kinetic effects. On increasing the molecular weight of a polymer, both glassy, crystalline and liquid crystalline transition temperatures increase up to a certain molecular weight beyond which they become almost molecular weight independent. This has been demonstrated to be the case for both crystalline (14) and liquid crystalline (5, 11, 15, 16) phase transition temperatures displayed by side chain liquid crystalline polymers. This represents a thermodynamic effect, which was explained by Finkelmann et al (16) for liquid crystalline polymers.

In the case of side chain liquid crystalline polymers, thermal transition temperatures are most frequently molecular weight independent above $\bar{M}n$ = 10,000 (5, 11, 15, 16). Therefore, phase transitions of liquid crystalline polymers containing different polymer backbones can be quantitatively compared only when their molecular weights are above this value. Only 4-6-PMA and 4-6-PS from Table I have molecular weights within the range where their phase transitions are molecular weight independent. Nevertheless, for the purpose of this discussion we will consider all these polymers at least in a qualitative manner.

Let us remember that crystalline phase transitions are kinetically controlled while liquid crystalline transitions are thermodynamically controlled. Therefore, we might expect a

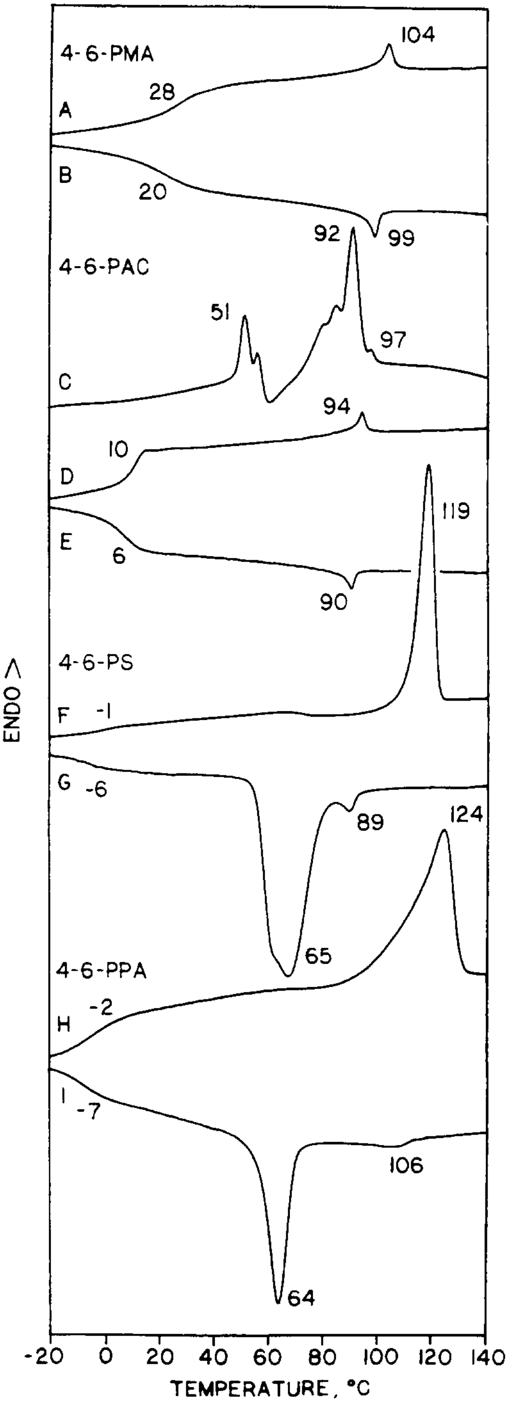
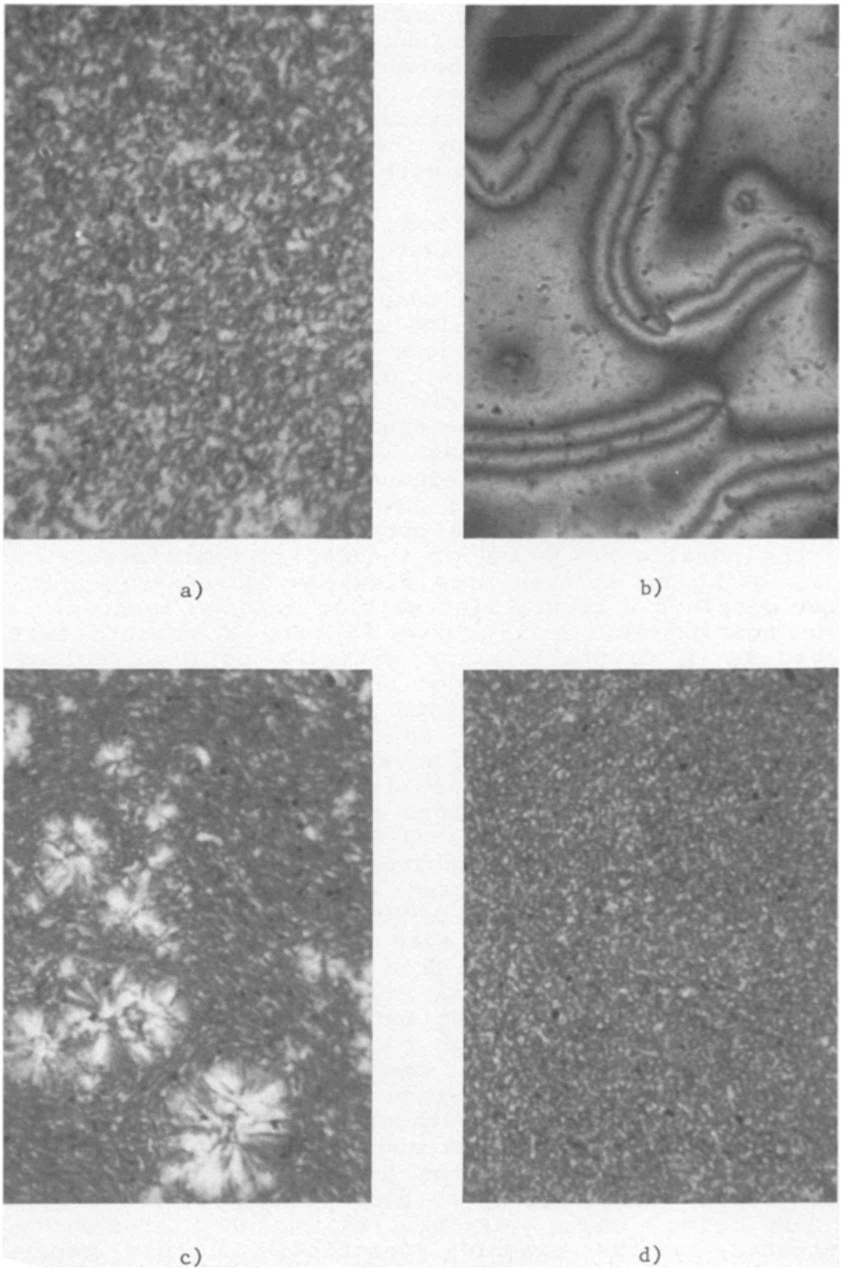


Figure 1. Normalized DSC traces (20°C/min) of: A) 4-6-PMA, second and subsequent heating scans; B) 4-6-PMA, first and subsequent cooling scans; C) 4-6-PAC, first heating scan or second heating scan after annealing above T_g; D) 4-6-PAC, second and subsequent heating scans; E) 4-6-PAC, first and subsequent cooling scans; F) 4-6-PS, second and subsequent heating scans; G) 4-6-PS, first and subsequent cooling scans; H) 4-6-PPA, second and subsequent heating scans; I) 4-6-PPA, first and subsequent cooling scans.

stronger effect derived from the polymer backbone flexibility on crystalline phase transitions than on liquid crystalline phase transitions. We can assume that the conformation of a flexible backbone can be easily distorted, and therefore, allows an easier pathway towards crystallization or liquid crystalline phase formation by the polymer side groups than in the case of polymers based on more rigid backbones.

Representative heating and cooling DSC curves for all polymers are presented in Figure 1. All display a nematic mesophase and those based on flexible backbones present also side-chain crystallization. Independent of the thermal history of the sample, 4-6-PMA exhibits only an enantiotropic nematic mesophase (curves A, B in Figure 1). 4-6-PAC, which is based on a more flexible backbone, displays multiple crystalline meltings only in the first heating scan (Figure 1C). Subsequent cooling and heating scans present only an enantiotropic nematic mesophase (curves D and E). Annealing above the T_g of 4-6-PAC, reinduces side chain crystallization, and the following DSC heating scan resembles the first heating scan. Nevertheless, even as obtained from the first heating scan, the nematic mesophase of 4-6-PAC is enantiotropic (Table I). On going to an even more flexible backbone (4-6-PS), the polymer displays a crystalline melting into an isotropic liquid on the heating DSC scan (curve F), and a nematic mesophase followed by a crystallization exotherm on the cooling scan (curve G). The crystallization and melting processes are less dependent on the thermal history of the sample i.e., less kinetically controlled than in the case of the previously discussed polymers containing more rigid backbones. Therefore, 4-6-PS has a melting transition temperature above the nematic-isotropic transition temperature and therefore displays only a monotropic nematic mesophase. 4-6-PPA behaves similarly to 4-6-PS, i.e., it displays a monotropic nematic mesophase (curves H and I). As in the case of 4-6-PS, the side chain crystallization ability of 4-6-PPA is very high in comparison to that of polymers based on more rigid polymer backbones.

The results obtained from these experiments are in agreement with the discussion in the introduction. That is, the more flexible the polymer backbone, the more able are side groups to crystallize or form liquid crystalline phases, or in other words, the higher the degree of decoupling. These results are very important since they demonstrate that for a certain mesogenic unit and spacer length, the nature of the polymer backbone dictates the degree of decoupling. The most flexible backbone provides the highest degree of decoupling. Nevertheless, a high degree of decoupling provides also a high rate of side chain crystallization and therefore, as illustrated by the examples described in this paper, may transform an enantiotropic mesophase into a monotropic mesophase. These examples demonstrate how kinetically controlled side chain crystallization influences the thermodynamically controlled mesomorphic phase through the flexibility of the polymer backbone.



a)

b)

c)

d)

<u>Figure 2</u>. Optical polarized micrographs (100X) obtained on cooling from the isotropic state of: a) 4-6-PMA, after 0.5 hr at 101°C; b) 4-6-PAC, after 0.5 hr at 89°C; c) 4-6-PS, after 30 sec at 91°C; d) 4-6-PPA, after 0.5 hr at 108°C.

Some representative nematic textures displayed by these polymers are shown in Figure 2. The dynamics of mesophase formation also provide qualitative information on the degree of decoupling. On cooling from the isotropic phase, 4-6-PMA shows a very fine nematic texture which requires a long annealing time to coarsen (Figure 2a). 4-6-PAC enters into the nematic mesophase by displaying a texture similar to that of 4-6-PMA. However, it coarsens very quickly and forms a Schlieren nematic texture with very few disclination lines (Figure 2b). 4-6-PS displays a metastable nematic texture. The polymer crystallizes from the nematic mesophase with formation of spherulites and very quickly freezes the coarsening of the nematic texture (Figure 2c). 4-6-PPA's nematic texture can not develop very well, since the nematic phase is metastable and the polymer undergoes side chain crystallization. Due to the lower flexibility of the polyphosphazene backbone compared to the polysiloxane one, this polymer does not crystallize with formation of spherulites (Figure 2d).

Mesomorphic transition temperatures displayed by these polymers can not be compared, due to large differences in the polymer molecular weights. However, enthalpy and entropy changes associated with these thermal transitions can be compared since they are molecular weight independent (11). Unexpectedly, the largest enthalpy and entropy changes associated with the nematic-isotropic transition are displayed by the polymers with the most rigid backbone. These thermodynamic data contradict the trend observed in the relationship between polymer backbone flexibility and degree of decoupling. The entropy changes associated with the isotropic-nematic phase transition (Table I) suggest that the polymers containing the most rigid backbones display a higher degree of order in the mesomorphic state than the polymers based on flexible backbones. This data agrees with other results obtained in our laboratory on different side chain liquid crystal polymers (17). An attempt to explain this behavior based on the difference between the conformations of flexible and rigid polymer backbones will be provided in an other publication.

ACKNOWLEDGEMENTS

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