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Effect of Backbone Flexibility on the Thermal Properties of Side-Group Liquid-Crystal Polymers

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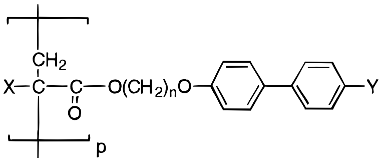
ABSTRACT: A new series of side-group liquid-crystal polymers, the poly[ω-(4-methoxybiphenyl-4′-yloxy)alkyl acrylate]s, has been synthesized in which the spacer length is varied from 3 to 12 methylene units. The thermal behavior of the polymers has been characterized using differential scanning calorimetry and polarized light microscopy. All 10 homologues exhibit thermotropic liquid crystalline behavior. The glass transition temperatures decrease initially before reaching a limiting value as the spacer length is increased. This is attributed to a plasticisation of the backbone by the side groups. A small odd−even effect in the clearing temperatures is observed on increasing the spacer length in which the odd members display the higher values. The properties of these polymers are compared to the analogous polymethacrylate-based materials and also to the corresponding polymers containing 4-cyanobiphenyl as the mesogenic unit. This reveals that the structure of the liquid-crystal phase influences the glass transition temperature. Thus, the 4-methoxybiphenyl-containing polymers exhibit the higher glass transition temperatures reflecting the higher packing density observed in the smectic phases exhibited by these polymers when compared to the interdigitated phases exhibited by 4-cyanobiphenyl-containing polymers. A comparison of the clearing temperatures reveals that the expected trend in which the more flexible backbones exhibit the higher clearing temperatures is not found. It is suggested that for the 4-methoxybiphenyl-based polyacrylates the clearing transitions may be entropically driven whereas for interdigitated phase structures the clearing transitions are driven by the interaction between the 4-cyanobiphenyl units.

Introduction

Side-group liquid-crystal polymers (SGLCPs) have considerable application potential in a range of advanced electrooptic technologies.[1] At the root of this potential is the unique duality of properties exhibited by SGLCPs; specifically, a combination of macromolecular characteristics such as mechanical integrity and ease of processability, with the electrooptic properties, albeit on a much slower time scale, of low molar mass liquid crystals. A great many SGLCPs with differing structures have been reported in the literature, and by comparison of their transitional behaviors, empirical rules have been devised relating molecular structure to liquid-crystalline behavior.[2,3] For example, it is widely believed that increasing the backbone flexibility while keeping the spacer and mesogenic groups constant has two main effects: (i) the clearing temperature of the polymer increases and (ii) the entropy change associated with the clearing transition decreases.[4,5] These rules, however, have been established only for a limited range of backbones, primarily with 4-cyanobiphenyl as the mesogenic group.[6] To establish if these rules can be extrapolated to other backbones and mesogenic groups, we have now synthesized the poly[ω-(4-methoxybiphenyl-4′-yloxy)alkyl acrylate]s (**1**) (see Figure 1). The acronym PA-*n* is used to refer to these polymers in which *n* denotes the number of methylene units in the spacer. The length of the spacer has been varied from 3 to 12 methylene units, and we believe that this is the most complete homologous series of polyacrylate-based side-group liquid-crystal polymers to be reported. 4-Methoxybiphenyl was chosen as the mesogenic group for two reasons: (i) 4-methoxybiphenyl-based materials tend to exhibit monolayer smectic phases as opposed to the interdigitated structures observed for polymers containing 4-cyanobiphenyl, and thus the role of phase structure in determining transitional properties can be investigated; (ii) we have reported the transitional properties of the analogous polymethacrylate-based series, the poly[ω-(4-methoxybiphenyl-4′-yloxy)alkyl methacrylate]s (**2**)[7] (see Figure 1), and this allows for the effects of backbone flexibility to be considered. The acronym used to refer to series **2** is PMA-*n* in which *n* again refers to the number of methylene units in the flexible spacer.



Series	X	Y
PA-*n*	H	OCH_3
PMA-*n*	CH_3	OCH_3
CNPA-*n*	H	CN
CNPMA-*n*	CH_3	CN

Figure 1. Structures of the polymers and their acronyms.

Experimental Section

The PA-*n* series, **1**, was prepared using the synthetic route shown in Scheme 1. 4-Hydroxy-4′-methoxybiphenyl, **3**, was prepared using the modification to the procedure of Rodriguez and Percec[8] described in detail elsewhere.[7] Similarly the synthesis of the α-bromo-ω-(4-methoxybiphenyl-4′-yloxy)alkanes, **4**, has been given elsewehere.[7] Identical procedures were used to prepare all members of the ω-(4-methoxybiphenyl-4′-yloxy)alkyl acrylates, **5**, and of the PA-*n* series, and hence, only representative syntheses are provided. α,ω-Dibromoalkanes (Aldrich) were distilled under reduced pressure prior to use. Benzene and tetrahydrofuran (THF) were distilled over calcium hydride. AIBN was purified by recrystallization from

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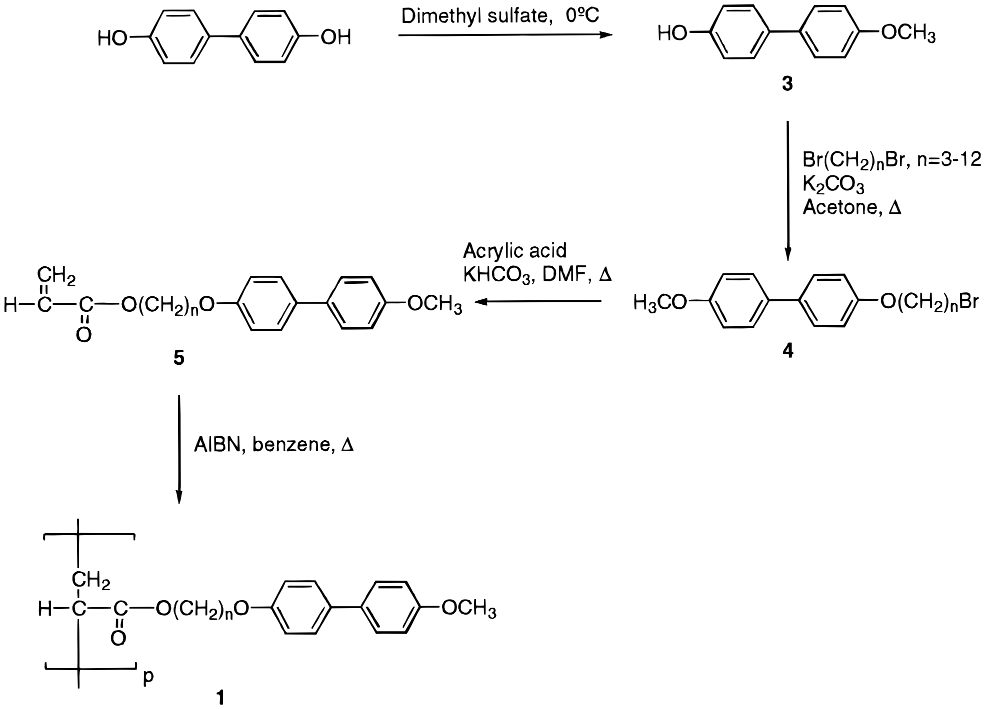
Scheme 1



toluene, washed with petroleum spirits (80−100 °C), and dried under vacuum. All other reagents were used as received.

6-(4-Methoxybiphenyl-4′-yloxy)hexyl Acrylate, 5 (*n* = 6). **5** (*n* = 6) was prepared using the procedure described by Craig and Imrie.[7] Acrylic acid (0.37 g, 5.1 mmol) was stirred with potassium hydrogen carbonate (0.5 g, 5.0 mmol) at room temperature for 5 min to form the potassium acrylate salt. To this was added **4** (*n* = 6) (1.5 g, 4.1 mmol), hydroquinone (0.0081 g, 0.08 mmol), and *N*,*N*′-dimethylformamide (100 mL), and the reaction mixture was stirred at 100 °C overnight. On cooling, the reaction mixture was added to water (ca. 300 mL) and stirred. The resulting precipitate was collected and dissolved in dichloromethane. This solution was washed with 5% aqueous sodium hydroxide and subsequently with water. The organic layer was dried over anhydrous magnesium sulfate and the solvent removed. The product was recrystallized twice from ethanol.

Yield: 1.2 g, 84%. Melting point: 92.1 °C.

IR (KBr), ν/cm^{-1}: 1736 (vs C=O), 1633 (C=C).

^{1}H NMR (CDCl$_3$), δ: 6.9, 7.5 (m, 8H, aromatic), 6.4 (q, 1H, H_2C=CH trans), 6.1 (q, 1H, $H_2C{=}CH$), 5.8 (q, 1H, H_2C=CH cis), 4.2 (t, 2H, J = 6.6 Hz, $H_2COC(O)$), 4.0 (t, 2H, J = 6.4 Hz, OCH_2), 3.8 (s, 3H, OCH_3), 1.6−1.9 (m, 4H, OCH_2CH_2, CH_2-$CH_2OC(O)$), 1.3−1.6 (m, 4H, $O(CH_2)_2(CH_2)_2(CH_2)_2OC(O)$).

Poly[ω-(4-methoxybiphenyl-4′-yloxy)alkyl acrylate], 1. Monomer **5** (ca. 1 g) was dissolved in benzene (10 mL) and 1 mol % AIBN added as initiator. The reaction mixture was flushed with argon for 20 min and then heated in a water bath at 60 °C to initiate the polymerization. After 72 h the reaction was terminated on addition of THF (15 mL) and the polymer was precipitated into a large amount of methanol. The product was then redissolved into chloroform and reprecipitated into methanol. The removal of the monomer from the polymer was monitored spectroscopically by the disappearance of both the alkene stretch at 1633 cm^{-1} in the IR spectra and the peaks associated with the alkene protons at 5.8 and 6.1 ppm in the ^{1}H NMR spectra of the monomer.

PA-6 Yield: 0.56 g, 52%.

IR (KBr), ν/cm^{-1}: 1733 (vs C=O)

^{1}H NMR (CDCl$_3$), δ: 6.9, 7.4 (m, 8H, aromatic), 3.8−4.1 (m, 4H, OCH_2), 3.7 (s, 3H, OCH_3), 2.2 (m, 1H, CH), 1.2−1.8 (m, 10H, CH_2)

Characterization. The proposed structures of all the compounds were verified using ^{1}H NMR and IR spectroscopy. ^{1}H NMR spectra were measured in CDCl$_3$ on a Bruker AC−F 250 MHz NMR spectrometer. IR spectra were recorded using a Nicolet 205 FTIR spectrometer. The molecular weights of the polymers were measured by gel permeation chromatography using a Knauer Instruments chromatograph equipped with two PL gel 10 μm mixed columns and controlled by Polymer Laboratories GPC SEC V5.1 software. THF was used as the eluent. A calibration curve was obtained using polystyrene standards.

The thermal properties of the polymers were determined by differential scanning calorimetry (DSC) using a Polymer Laboratories PL-DSC equipped with an autocool accessory and calibrated using an indium standard. Two samples were used for each polymer and the results averaged. The time−temperature profile for each was identical. Thus, each sample was heated from 25 to 200 °C, maintained at 200 °C for 3 min, cooled to −50 °C, maintained at −50 °C for 3 min, and finally reheated to 200 °C. The heating and cooling rate in all cases was 10 °C min^{-1}. Phase identification was performed by polarized light microscopy using an Olympus BH-2 optical microscope equipped with a Linkam THMS 600 heating stage and TMS 91 control unit. Clear, characteristic optical textures from which phase assignments were possible were obtained by cooling at either 0.2 or 0.1 °C min^{-1} from ca. 10 °C above the clearing temperature to below the glass transition temperature or, in the absence of glassy behavior, to room temperature. The structures of selected phases were studied further using X-ray diffraction, for which a Philips PW 1080 goniometer with a PW 1710 control unit and a post-sample graphite monochromator was used. X-ray samples were scanned at a rate of 6° 2ϑ min^{-1}.

Results and Discussion

Table 1 lists the molecular weights, number-average degrees of polymerization and the polydispersities of the PA-*n* series **1**. The number-average molecular weights range from 6500 to 13 000 with associated number-average degrees of polymerization in the range 15−38. Although these values appear to be rather low, it has been shown that the transition temperatures of polyacrylate-based side-group liquid-crystal polymers become molecular weight independent at degrees of po-

Table 1. Molecular Weights, Associated Polydispersities (PD), and Number Average Degrees of Polymerization (DP) for the PA-*n* Series, 1

n	$\bar{M}_n$	$\bar{M}_w$[1]	PD	DP
3	9600	29 200	3.04	31
4	10 300	31 700	3.07	32
5	13 000	29 800	2.29	38
6	12 900	30 100	2.32	37
7	7600	13 400	1.77	21
8	7900	16 500	2.10	21
9	8800	13 500	1.54	22
10	7800	15 600	1.99	19
11	8600	13 300	1.56	20
12	6500	9700	1.50	15

lymerization in the range 12−40.[9−11] Within this regime the molecular weight dependence of the transition temperatures is initially strong but rapidly decreases. In general, the molecular weights of polyacrylate-based SGLCPs are lower than the analogous polymethacrylate-based materials prepared under identical conditions and the yields of the latter tend to be significantly higher.[10] The data for series **1** and **2**[7] are in accord with these general observations which may be rationalized in terms of the higher reactivity of the acrylate monomers and possible increased chain transfer processes.[12] Thus, the molecular weights of the PA-*n* series may place the thermal behavior of selected members of the series on the border between the molecular weight dependent and independent regimes, but not in the regime in which the transition temperatures are strongly dependent on molecular weight.

The thermal properties of the PA-*n* series, **1**, are listed in Table 2. These data have been extracted from the second heating cycles of the DSC time−temperature profile and the traces are collected in Figure 2. The DSC trace for PA-3 contains only an endotherm (see Figure 2). When PA-3 is cooled from the isotropic phase, a poorly defined focal conic fan texture was observed when viewed through the polarized light microscope. This is assigned as a smectic A phase, although the entropy change associated with the clearing transition is somewhat higher than that normally observed for the smectic A-isotropic transition. PA-4 also exhibits a single endothermic peak in the DSC trace, but when it is cooled from the isotropic phase, a combined isotropic−nematic−smectic transition is observed. The width of the nematic phase is, however, too narrow (<1 °C) to be resolved in the DSC trace. A well-defined focal conic fan texture is obtained for PA-4, and thus, the phase is assigned as smectic A.

The DSC trace for PA-5 shows two endothermic peaks and a weak second-order transition (see Figure 2). The latter transition is assigned as a glass transition but is too small to be seen on the scale used in Figure 2. When PA-5 is cooled from the isotropic phase, bâtonnets develop which coalesce to give a well-defined focal conic fan texture indicative of a smectic A phase. When it is cooled to temperatures below that associated with the second endothermic peak, continuous bands appear across the backs of the fans which persist to room temperature. This is characteristic of an E−smectic A phase transition. The DSC trace for PA-6 is similar to that described for PA-5, but the higher temperature peak has a small shoulder at ca. 142 °C. When PA-6 is cooled from the isotropic phase, a narrow nematic phase is observed which precedes the development of a well-defined focal conic fan texture at temperatures below that associated with the shoulder of the endotherm. The lower temperature phase is thus assigned as a smectic A phase. The clearing endotherm in the DSC trace represents, therefore, a combined isotropic−nematic−smectic transition analogous to that exhibited by PA-4. When is is cooled further, continuous bands develop across the backs of the fans which persist until room temperature; in consequence, the lower temperature phase is assigned as an E phase.

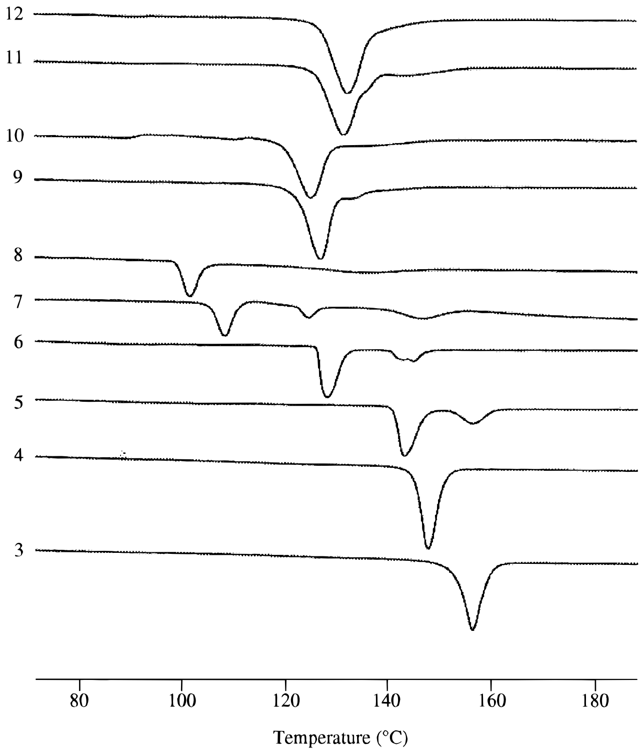


Figure 2. Normalized DSC traces obtained on the second heating of the PA-*n* series, **1**.

The DSC trace of PA-7 is the most complex of the series (see Figure 2) and contains a weak glass transi-

Table 2. Thermal Properties of the PA-*n* Series, 1

n	T_g/°C	T_{SS}/°C	T_{SI}/°C	ΔH_{SS}/kJ mol^{-1}	ΔH_{SI}/ kJ mol^{-1}	$\Delta S_{SS}/R$	$\Delta S_{SI}/R$
3			156		8.73		2.45
4	110		148[a]		9.18[a]		2.62[a]
5	88	143	156	5.77	2.02	1.67	0.56
6	77	128	145[a]	5.79	1.80[a]	1.74	0.52[a]
7	57	107, 124[d]	145	4.11, 1.76[d]	2.56	1.30, 0.53[d]	0.74
8	56	101	135	4.06	2.41	1.31	0.71
9		127	133[b]		16.51[c]		4.89[c]
10		125	137[b]		16.12[c]		4.73[c]
11	48	132	144[b]		21.73[c]		6.27[c]
12	51		132		22.15[c]		6.58[c]

[a] A combined S−N−I transition. [b] Appears as a shoulder on main endothermic peak. [c] Combined transition. [d] Crystal phase.

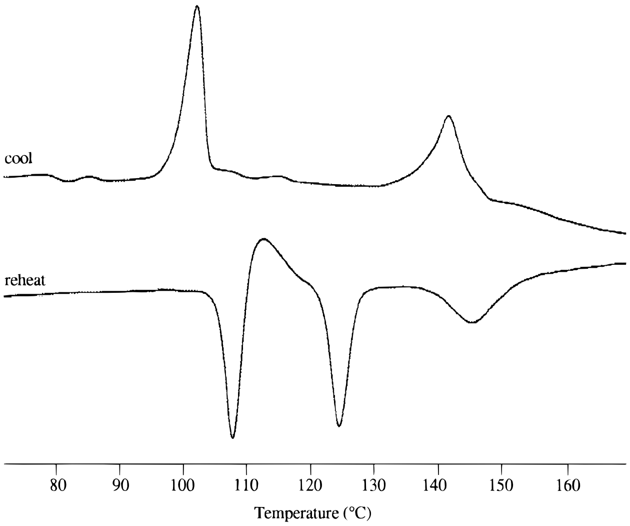


Figure 3. Cooling and reheating cycles of the DSC trace for PA-7.

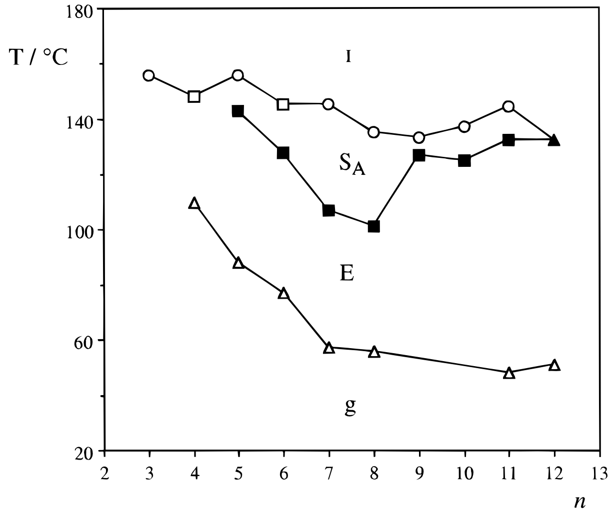


Figure 4. Dependence of the transition temperatures on varying the length of the alkyl spacer, *n*, for the PA-*n* series: glass transition temperatures (△); combined E−smectic A−isotropic (▲); smectic A−isotropic (○); combined smectic−nematic−isotropic (□); E−smectic A (■). Crystal transitions have been omitted. Key: I, isotropic; S_A, smectic A; E, crystal E; g, glass.

tion, three endothermic peaks at 107, 124, and 145 °C and an exotherm between the two lower temperature endotherms. When PA-7 is cooled, the endotherm at 124 °C is absent (see Figure 3). The initial heating trace of this sample contains two endothermic peaks at 124 and 144 °C. The extensive supercooling of the transition associated with the endotherm at 124 °C strongly suggests that this is a melting transition, a view supported by the observation of cold crystallization on reheating. When the sample is cooled from the isotropic phase to temperatures below 145 °C, a well-defined focal conic fan texture develops, which is assigned as a smectic A phase. When it is cooled further, bands developed across the backs of the fans at ca. 107 °C indicative of an E phase. When it is annealed, small cracks developed in the texture, suggesting that crystallization had occurred. The phase sequence on cooling is isotropic−smectic A−crystal E and partial crystallization while when it is reheated, the E−smectic A transition is followed by cold crystallization, the crystal−smectic A transition, and, finally, the clearing transition.

The DSC trace of PA-8 showed a weak glass transition and two endothermic peaks. When PA-8 is cooled from the isotropic phase, a poorly defined focal conic fan texture develops, and this is assigned as a smectic A−isotropic transition. The entropy change associated with this phase transition ($\Delta S/R = 0.71$) is in agreement with this assignment. When the sample is cooled further, bands develop across the backs of the fans indicating an E−smectic A phase transition.

No glass transitions were apparent in the DSC traces of PA-9 and PA-10, and just a single endotherm possessing a high temperature shoulder was observed; the principle endotherm for each polymer exhibits extensive supercooling, revealing the shoulder as a separate peak which does not undercool to any significant extent. The temperatures associated with the shoulders correspond to the clearing points of the polymers. PA-9 and PA-10 exhibited similar optical textures; specifically, when they are cooled from the isotropic phase, a well-defined focal conic fan texture is obtained, and this is assigned as a smectic A−isotropic phase transition. When they are cooled further, the focal conic fans become banded, suggesting an E−smectic A transition although small cracks are visible in the preparations which when combined with the supercooling strongly suggests crystallization is occurring in these samples. By comparison, the endotherm associated with the clearing transition does not undercool, indicating the existence of a liquid-crystal phase transition. PA-11 exhibits behavior identical to those of PA-9 and PA-10 except a glass transition is detected by DSC; the transition temperatures listed in Table 2 for PA-11 are in good agreement with those reported by Hsu et al.[13] The DSC trace for PA-12 shows a glass transition and an endotherm (see Figure 1) which exhibits extensive supercooling. The optical textures obtained for this sample were similar to those described for PA-9 and PA-10. The absence of a high temperature shoulder on the endothermic peak in the DSC trace may be attributed to the narrow temperature range of the smectic A phase observed optically.

Figure 4 shows the dependence of the transition temperatures when the number of methylene units in the alkyl spacer is increased for the PA-*n* series. The glass transition temperatures initially decrease before reaching a limiting value of *ca.* 50 °C. This decreasing trend suggests a plasticization of the polymer backbone by the side chains. A small odd−even effect in the clearing temperature can be seen with the odd members exhibiting the higher values. This may be rationalized by considering the average shape of the side chains as the spacer length and parity is varied and its effect on the relative orientation of the mesogenic groups.[2,4] It is difficult to comment on the dependence of the entropy change associated with the clearing transition on the number of methylene units in the spacer because many of the entropies represent combined transitions, although the values exhibited by $n = 9-12$ are high and indicative of the presence of crystallinity.

To establish the effects of backbone flexibility on the transitional properties of SGLCPs, Figures 5 and 6 compare the glass transition temperatures and clearing temperatures, respectively, of the polyacrylate-based PA-*n* series, **1**, and the polymethacrylate-based PMA-*n* series, **2**.[7] Figures 5 and 6 also show the transition temperatures for the analogous polymers containing 4-cyanobiphenyl as the mesogenic unit, i.e., the poly[ω-(4-cyanobiphenyl-4′-yloxy)alkyl acrylate]s[14−25] and

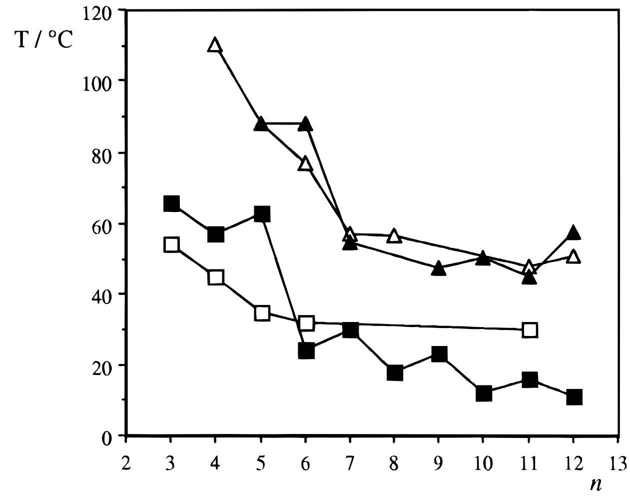


Figure 5. Dependence of the glass transition temperatures for the PA-*n* (△), PMA-*n* (▲), CNPA-*n* (□), and CNPMA-*n* (■) series, on the number of methylene groups, *n*, in the spacer.

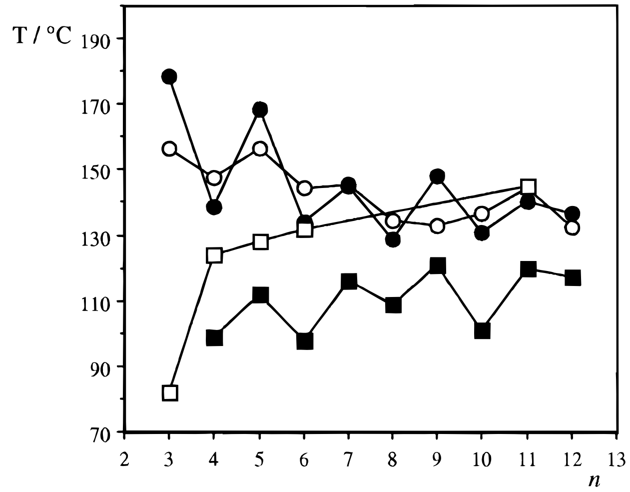


Figure 6. Dependence of the clearing transition temperatures for the PA-*n* (○), PMA-*n* (●), CNPA-*n* (□), and CNPMA-*n* (■) series, on the number of methylene groups, *n*, in the spacer.

the poly[ω-(4-cyanobiphenyl-4′-yloxy)alkyl methacrylate]s;[6] the acronyms used to refer to these series are CNPA-*n* and CNPMA-*n*, respectively (see Figure 1). For all four series of polymers, the glass transition temperature tends to decrease as the length of the flexible alkyl spacer increases, see Figure 5. This decreasing trend implies a plasticisation of the polymer backbone by the side groups. On the basis of backbone flexibility alone, it would be expected that the series based on the more flexible polyacrylate backbone would yield side-group liquid-crystal polymers having lower glass transition temperatures than the analogous polymethacrylate-based materials. This expectation is not realized, however, and the glass transition temperatures of the corresponding polyacrylate and polymethacrylate-based materials are remarkably similar. The glass transition temperatures of the polymers containing 4-methoxybiphenyl as the mesogenic unit are higher than those of the polymers containing 4-cyanobiphenyl. Thus, it is clear that the glass transition temperatures are not determined solely by the nature of the backbone. We will return to this observation later.

Figure 6 shows the dependence of the clearing temperature on the length of the alkyl spacer, *n*, for each series. This figure compares smectic−isotropic and nematic−isotropic transitions, which is a valid approach because it is generally found that, for a given homologous series in which a switchover from nematic to smectic behavior occurs, the trend in the smectic−isotropic transition temperatures parallels that for the nematic−isotropic transition temperatures. Hence the shape of the clearing temperature curve does not depend, in general, on the type of transition being considered.[26] The CNPA-*n* series exhibits higher clearing temperatures than the CNPMA-*n* series. This behavior is consistent with the view that increasing backbone flexibility enhances the clearing temperature. In comparison, the clearing temperatures for the PMA-*n* and PA-*n* series do not exhibit the expected trend. Specifically, the even members of the PA-*n* series show higher clearing temperatures than the corresponding member of the PMA-*n* series, but this is reversed for odd members. Thus, the alternation in the clearing temperatures for the PMA-*n* series is more pronounced than that for the PA-*n* series. In an attempt to understand this behavior as well as the trends observed in the glass transition temperatures, the smectic phase structures of two of the odd members of the PA-*n* series, PA-3 and PA-5, were studied using X-ray diffraction. The layer spacings for PA-3 and PA-5 were measured to be 21.3 and 24.4 Å, respectively, while for the corresponding members of the PMA-*n* series, i.e., PMA-3 and PMA-5, the smectic periodicities are 20.9 and 24.3 Å, respectively. These layer spacings are comparable to the estimated length of the side groups, and thus, the polymethacrylate and polyacrylate-based series exhibit similar S_{A1} type structures in which the side groups are fully interleaved. In comparison, the 4-cyanobiphenyl-based polymers exhibit the interdigitated S_{Ad} phase in which the side groups only partially overlap.

If we now return to the glass transition temperatures, see Figure 5, it is clear that the higher glass transition temperatures are observed for polymers which exhibit smectic phases in which the side groups are fully overlapped. Specifically, the two 4-methoxybiphenyl-containing series, which exhibit S_{A1} phases, show higher glass transition temperatures than the analogous 4-cyanobiphenyl-containing materials, which form S_{Ad} phases. A similar relationship between phase structure and the glass transition temperature has been noted for polystyrene-based materials.[27] The packing density is higher in the smectic phases exhibited by the 4-methoxybiphenyl-containing series, and hence, there is a reduction in the specific free volume in the smectic phase when compared with the interdigitated arrangement exhibited by the corresponding 4-cyanobiphenyl-containing polymer. This reduction in the specific free volume accounts, therefore, for the higher glass transition temperatures.

We now turn our attention to the relationship between polymer structure and the clearing temperature. Given that the PMA-*n* and PA-*n* series exhibit the same modification of the smectic A phase and that the spacer and mesogenic groups in each are identical, the differences in phase behavior and in the transition temperatures must be related to the flexibility of the backbone. The PA-*n* series has a tendency to exhibit more highly ordered smectic and crystal phases than the PMA-*n* series. It is well-known for conventional polymers that the melting process tends to be entropically driven.[28] Thus, flexible backbones tend to exhibit lower melting temperatures than more rigid backbones. It is reasonable to assume, therefore, that the clearing temperatures of the PA-*n* series may also be entropically driven and this would explain why these are lower than expected. In comparison, for S_{Ad} phases, the driving force is the electrostatic interaction between the polar and polarizable 4-cyanobiphenyl groups and is determined largely by the ability of the mesogenic groups to interact. Thus, for 4-cyanobiphenyl-containing polymers, the clearing temperature increases with backbone flexibility, which facilitates the mesogen−mesogen interactions. Therefore, the relationship between the clearing temperature and backbone flexibility depends, at least in part, on the nature of the liquid-crystalline phase. For highly organized phases, increasing backbone flexibility appears to decrease the clearing temperature while for interdigitated phases increasing backbone flexibility increases the clearing temperature.

This rationalization of the unusual behavior observed in Figure 6 accounts, also, for the apparently anomalous behavior observed for polysiloxane-based materials containing 4-methoxybiphenyl.[29,30] The propyl and butyl homologues of this series have been reported to be crystalline in nature, exhibiting crystal−isotropic transition temperatures at 125 and 123 °C, respectively.[30] This is surprising because the highly flexible polysiloxane chain would be expected to yield higher clearing temperatures than the analogous members of the PA-*n* or PMA-*n* series. The undecyl member ($n = 11$) of the series[29] exhibits a smectic−isotropic transition at 154 °C, which should be compared to either PA-9 or PMA-9, as it is the total number of atoms contributing to the length of the spacer that must be considered. The clearing temperature of the polysiloxane-based material is 21 °C higher than that exhibited by PA-9 and 6 °C higher than PMA-9. These moderate increases in the clearing temperature are not as large as expected, however, on the basis of 4-cyanobiphenyl-containing polymers.[6,31] These results may now be understood, however, within a framework in which the clearing transitions for polymers containing flexible backbones and highly ordered smectic and/or crystal phases are entropically driven.

Conclusions

A comparison of the thermal properties of polyacrylate and polymethacrylate-based SGLCPs containing either 4-methoxybiphenyl or 4-cyanobiphenyl as the mesogenic group has shown that the glass transition temperature is not solely determined by the flexibility of the backbone. Instead, the nature of the liquid-crystalline phase also has an influence; for example, the 4-methoxybiphenyl-containing polymers, which exhibit S_{A1} type phases, exhibit higher glass transition temperatures than the corresponding polymers containing 4-cyanobiphenyl, which exhibit interdigitated phases. This is attributed to the difference in the specific free volume between these phases. Similarly, the relationship between the clearing temperature and backbone flexibility depends also on the nature of the liquid-crystalline phase. Specifically, for highly organized phases, increasing backbone flexibility appears to decrease the clearing temperature, presumably implying an entropically driven process, whereas for interdigitated phases increasing backbone flexibility increases the clearing temperature. Thus, caution must always be exercised when extrapolating empirical rules developed principally for one set of materials to another set exhibiting differing phase structures.

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