Influence of backbone tacticity on thermotropic properties of side chain liquid crystal polymethacrylates

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In order to study the tacticity effect of the backbone on the thermotropic properties of side-chain liquid crystalline (SCLC) polymers, the synthesis of four polymethacrylates with different tacticities and bearing methoxy biphenyl mesogenic groups was carried out. Homopolymers were obtained upon photopolymerisation at low temperature of two mesogenic methoxy biphenyl monomers, with and without ethylene oxide spacer. Methacrylic acid copolymers were obtained by grafting the same mesogenic groups onto 92% syndiotactic or atactic polymethacrylic acids. It is demonstrated that an increase of 11% of the content of syndiotactic triads compared to an atactic structure, does not modify the liquid crystal behavior of homopolymers. Indeed, smectic OB, A, E and nematic phases were identified as for similar atactic samples. On the other hand, with both copolymers, the liquid crystalline behavior disappears to the advantage of crystalline phases independently on the backbone configuration. The results confirm that mesogenic interactions govern the structural behavior of such polymethacrylate polymers. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polymethacrylates; photopolymerisation at low temperature; methacrylic acid)

INTRODUCTION

It is well known that the properties of side chain liquid crystalline (SCLC) polymers depend on the nature of the polymer backbone, the nature of the mesogenic groups and on the length of the flexible spacers[1]. However, little attention was given to the stereochemical configuration of the backbone, which is thought to be a factor influencing the microstructure, and thus the mesomorphic behavior of these polymers. Accordingly, a few articles deal with the tacticity effect of the backbone on the liquid crystal properties of these polymers. Frosini *et al.*[2] have shown that the organisation of isotactic and atactic poly(4-biphenylyl acrylate) were similar, with however, a substantial change in the transition temperatures. According to these authors, the interactions between the pendant groups are dominant and the main chain accommodates its conformation. In contrast, Hann *et al.*[3] studied the thermotropic properties of different polymethacrylates bearing methoxy-biphenyl side groups with alkyl spacers prepared by radical or anionic polymerisation. They contain respectively, 63% syndiotactic triads and 68% isotactic triads. They demonstrated that the 'smectic' crystal structure did not depend on the tacticity of the polymers but were unable to demonstrate the possible tacticity influence on the liquid crystalline state since, while optical studies showed smectic liquid crystalline textures for both samples, the diffraction diagrams resembled that of an amorphous polymer. Later on, Duran and Gramain[4]

proposed an interesting study on the same type of polymers with ethylene oxide spacers showing liquid crystalline phases. They observed that the content of syndiotactic fraction increases with the spacer lengths while the isotactic fraction decreases. In the single layer model proposed, the mesogenic groups hanged on the same side[5] of the main chain, an arrangement already observed with syndiotactic polymers in the crystalline state[6,7]. It was concluded that a high syndiotactic content must promote or make easier such ribbon-like arrangement.

In order to deepen the problem, we prepared four poly-(4′-methoxy-4-biphenylyl methacrylates) with different syndio triad contents. Two were prepared by photopolymerisation at low temperature of two monomers with and without an ethylene oxide spacer. The two others were prepared by grafting the mesogenic group without spacer onto an atactic and a syndiotactic polymethacrylic acid first prepared. The thermotropic properties of the four polymers are presented and discussed.

EXPERIMENTAL PART

4′-Methoxybiphenyl-4-ol and 2-{2-[2-(4′-ethoxy-4-biphenyloxy)ethoxy]ethoxy}-ethanol and their methacrylate derivatives (M-0 and M-3) were prepared from 4-4′-hydroxybiphenyl and 2-[2-(2-chloroethoxy)ethoxy]ethanol as described previously[4]. The four molecules were purified by silica column followed by recrystallisation in heptane. Purity was checked by thin layer chromatography and ^{1}H NMR as already described[4]. Atactic polymethacrylic acid from Polyscience ($\overline{M}_w = 10^5$) was used as received.

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Polymerisation

The two methacrylate monomers (M-0 and M-3) were photopolymerized in THF solution under N_2. Photopolymerisations (Candad-Hanovia) 941B0010 xenon/mercury were carried out in a double wall reactor (250 ml) equipped with a quartz window. In the following text, the homopolymers obtained will be referred by PM followed by two numbers indicating the number of ethylene oxide units and the mesogenic ratio respectively. For example, PM-3100 indicates a methacrylate polymer with three ethylene oxide units in the spacer and fully substituted by the biphenyl core. The grafted copolymers are indicated with the same expression but adding an A or a S relative to the atactic or syndiotactic backbone respectively

Homopolymers synthesis

Monomer M-3 $(1.5 \times 10^{-2} \text{ mol})$ and 0.12 g of 4,4′-azobis (4-cyanovaleric acid) (ACVA) were added to 150 ml of distilled THF. Nitrogen was bubbled through the stirred solution for 0.5 h and the reactor was irradiated for 38 h once the temperature of $-30°C$ was obtained. The crude polymer recuperated after evaporation of the solvent was dissolved in chloroform and precipitated in methanol, for at least 4 times. Yield after purification was approximately 20%. The same procedure was used for monomer M-0.

PM-0,100	Calc.	C 76,10	H 6,01	$\overline{M_w} = 2948$
	Found	C 77,0	H 6,53	$\overline{M_n} = 2035$
PM-3,100	Calc.	C 63,88	H 6,10	$\overline{M_w} = 97640$
	Found	C 64,10	H 6,40	$\overline{M_n} = 49130$

The molecular weights of the polymers were determined by light scattering at p/2 coupled with size exclusion chromatography in THF. For PM-O samples, the low degrees of polymerisation obtained were attributed to chain transfer to THF.

Synthesis of syndiotactic polymethacrylic acid

Freshly distilled methacrylic acid (Aldrich) (0.26 mol) and 0.26 mol of tetramethylammonium hydroxyde were added under nitrogen in a reactor cooled in an ice bath. Distilled water was added to obtain a monomer concentration of 10 wt.%. ACVA was added and the reactor was irradiated for 24 h once the temperature of $+5°C$ was obtained. The polymer was recovered by freeze drying, dissolved in 10 ml water, then the solution was neutralized with a 37% HCl solution. The precipitate of poly(-methacrylic acid) was dried, dissolved in 10 ml methanol and precipitated in methylene chloride for at least 4 times. Yield after purifications was approximately 45%. The molecular weight was determined from light scattering in methanol $(\overline{M_w} = 9.3 \times 10^4)$.

Copolymers synthesis

Syndiotactic polymethacrylic acid (5.8 mmol), was added to 30 ml of fresh pyridine. The solution was heated at 50°C until complete dissolution. Then, 2.14 ml of tributylamine, 8.7 mmol of 4-methoxy-4′-hydroxybiphenyl and 0.69 mmol of 4,4-dimethyl aminopyridine dissolved into 10 ml of pyridine were added to the previous solution. Dicyclohexyl carbodiimide (6.38 mmol), dissolved in 5.45 ml of fresh pyridine was added. The mixture was heated at 80°C for 5 h, then under reflux for 12 h. The solution was filtered and diluted with 50 ml of distilled water. The solution was neutralized with a HCl 37%

solution. The precipitate poly(4′-methoxy-4-biphenylyl methacrylate-alt-methacrylic acid) (PM-0,40S) was dried and purified with soxhlet of methanol. Yield after purification: 31%. The same procedure was used with atactic poly(methacrylic acid) (PM0,40A).

PM-0,40S	Found	C 73,76	H 7,36
PM-0,40A	Found	C 71,13	H 7,55

Ratios of grafting were calculated from the elemental analysis and the ^{1}H-NMR spectra. For both polymers, a $40 \pm 5\%$ ratio of grafting was obtained.

Polymer characterization

The polymers were characterized by elemental analysis and ^{1}H NMR spectroscopy. NMR spectra were taken in chloroform for (PM-0, PM-3), in methanol for poly-(methacrylic acid), and in pyridine for the copolymers with a Brucker 200 MHz apparatus. Microtacticity of the samples was determined from the relative intensities of the a-methyl resonance on the proton NMR spectra by deconvolution using the Pascal-Linesim software from Brucker. Isotactic contents were inferred from the syndiotactic and heterotactic contents. The molecular weights were obtained from light scattering in methanol and from SEC in THF.

Instrumentation

The polymorphic behavior of the polymers was obtained from differential scanning calorimetry (DSC) (Perkin-Elmer DSC-4) in sealed inox or aluminum pans using about 10 mg of sample. The measurements were systematically made at a series of heating and cooling rates of 20 K/min. Thermogravimetry was conducted on powdered samples using a Mettler TC10A instrument with a nitrogen vector gas. Typical textures were observed using a Zeiss polarizing optical microscope equipped with a Mettler FP 82 hot stage. X-ray diffraction was performed on a Debye-Scherrer camera, X-ray beam (CuKa) being produced by a rotating anode from Eliott.

RESULTS AND DISCUSSION

The polymers were prepared by photochemical polymerisation in THF of the respective monomers (PM-0,100 and PM-3,100), or by grafting onto an atactic and a syndiotactic polymethacrylic acid (PM-0,40A and PM-0,40S respectively). *Scheme 1* shows the corresponding chemical structures.

In order to increase the syndiotactic content of the two mesogenic polymethacrylate homopolymers, their radical

PM-n,100   n= 0 and 3

PM-0,xA and PM-0,xS
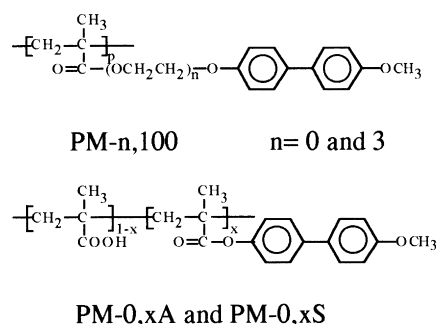
Scheme 1

photopolymerisation initiated by ACVA was carried out at −30°C in THF for M-0 and M-3 monomers. The syndiotactic polymethacrylic acid backbone was prepared by photopolymerisation of the tetramethylammonium salt monomer at +10°C in water. This method allows preparation of a highly syndiotactic structure by taking advantage of the repulsive interactions between the carboxylate anions promoting the racemic placement[8]. Esterification of the resulting syndiotactic polymethacrylic acid (PMMAc) and that of a commercial atactic PMMAc, was carried out in the same conditions using the DCC method in pyridine under reflux following a method described by Klesper et al.[9]. The esterification ratios were determined by elemental analysis and by ^{1}H NMR spectroscopy. Both methods indicate a ratio of 40 ± 5% for both polymers, a relatively low value in agreement with the results of Klesper. According to these authors, the grafting ratio is limited by the mechanism of reaction for which two consecutive carboxylic functions react together to form an anhydride able to react further with only one alcohol function. Our results confirm that the regenerated free carboxylic acid is poorly reactive, particularly towards bulky groups generating important steric effects. Such mechanism would lead to a preferential alternated arrangement, in which the mesogenic groups are randomly separated by none, one or two carboxylic acid groups. This particular structure will be considered later to interpret the structural properties of the copolymers.

Thermogravimetric measurements show thermal stability of these compounds to be quite good. Homopolymers and copolymers present the same behavior. They are stable up to 230–250°C, and above this temperature, a sudden weight loss occurs which is characteristic of the backbone degradation[10].

Stereoregularity of polymers

Table 1 shows the content of tacticity triads of the four prepared polymers together with the results of Ref. 4. They were determined by ^{1}H-NMR spectroscopy and deconvolution of the a-CH$_3$ peaks as illustrated on *Figure 1*. Results confirm the theoretical prediction showing that syndiotactic propagation in vinyl monomers is favored over isotactic propagation as the temperature of polymerisation is reduced. The calculated values for the additional probabilities of placement P(m/r) and P(r/m) for the methacrylate monomers reveal that the radical polymerisation of the mesogenic monomers deviates from the Bernoullian model, in contrast with the two samples prepared from methacrylic

acid and salt. The deviation is more important for the monomer without spacer namely M-0,100, confirming the results of Duran and Gramain[4] for which this behavior was due to the decreasing influence of the biphenyl-biphenyl interactions on the configuration adopted by the monomer as the spacer length is decreased.

Thermotropic properties

Typical textures of the polymers were determined upon optical polarizing microscopy. The textures of the two homopolymers obtained at low polymerisation temperature were found to be very similar to those obtained by polymerisation at 60°C[11]. Under the microscope, on cooling from the isotropic melt, the PM-3,100 sample with spacer turned out to be birefringent and a well developed texture appeared, identified as an ordered smectic organisation as shown in *Figure 2*. The optical study of the PM-0,100
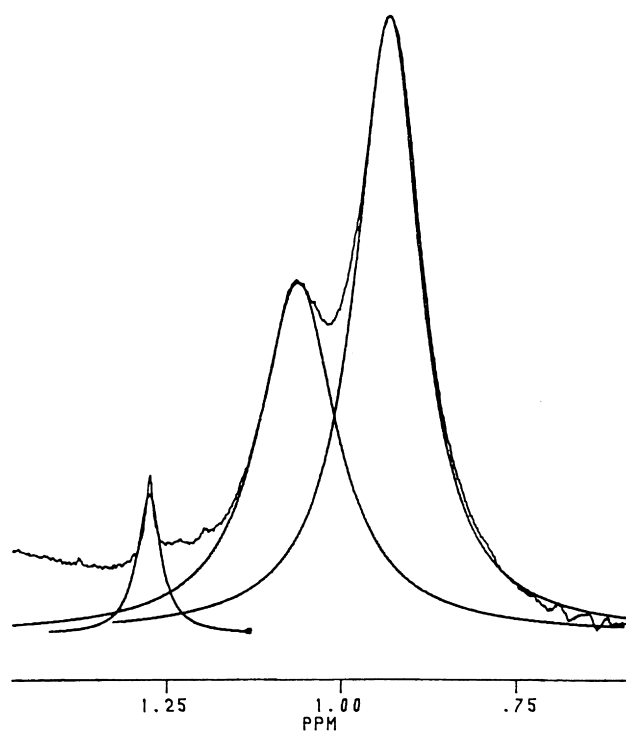

Figure 1 Example of deconvolution of a-methyl peaks for the PM-3,100 sample in CDCl$_3$

Table 1 Tacticity of the studied polymers

Samples	Polym. temp. °C	Tacticity triads (%)			P(m/r)	P(r/m)	P(m/r) + (P/rm) ± 5%
		rr (syndio)	± 1% mr (hetero)	mm (iso)			
PM-0,100	−30	50.1	33.6	16.4	0.50	0.25	0.75
PM-3,100	−30	59.5	33.6	6.9	0.71	0.22	0.93
PM0*	60	45.1	34.4	20.1	0.46	0.28	0.74
PM3*	60	53.7	34.7	11.2	0.61	0.24	0.84
PM-0, 40A		62.9	34.0	3.2	0.84	0.21	1.05
PM-0, 40S	+5	92.0	7.7	0.3	0.93	0.04	0.97

*Results from Duran and Gramain[4].

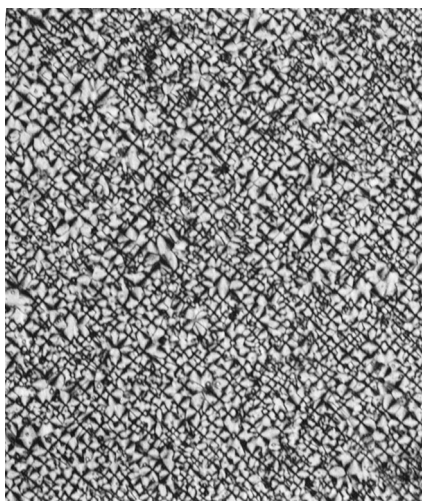$$P(m/r) = \frac{mr}{2mm + mr}; \; P(r/m) = \frac{mr}{2rr + mr}$$

Figure 2 Optical texture of PM-3,100 obtained at 96°C upon cooling from the isotropic state
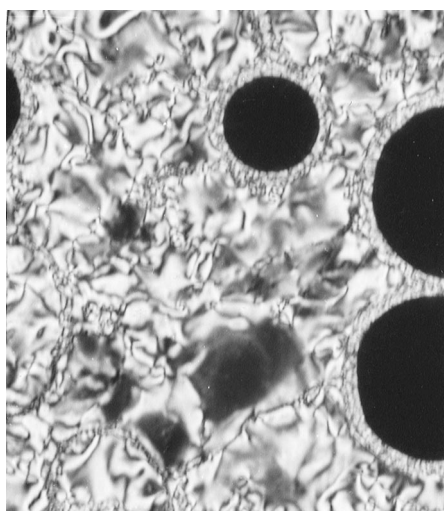

Figure 3 Schlieren texture of PM-0,100 obtained at 205°C upon heating

polymer without spacer was more complicated to perform due to its high viscosity as already noted[11]. On cooling from the melt, this polymer showed a typical fluid schlieren texture characteristic of a nematic liquid crystal phase (*Figure 3*). At lower temperatures, the texture changed very slowly leading to the formation of a fan texture which did not show any significant change on further cooling. Comparing the same polymers prepared at 60°C, it is clear that the tacticity modification induced by the polymerisation at −30°C does not disturb the optical textures of both liquid crystalline polymers.

The PM-0,40A and PM-0,40S copolymers were found to be optically anisotropic but their behavior was quite different. The syndiotactic sample appeared to be an anisotropic glassy solid from room temperature up to the beginning of its thermal decomposition at about 230°C, without any apparent change of texture. The atactic sample showed a behavior controlled by kinetic factors. During the first heating cycle, the sample is slightly birefringent up to 220°C, a temperature where the melting was observed together with the beginning of degradation. On cooling and after further cycles, the birefringence did not appear again. However, after annealing over a period of a few days at 130°C, the birefringent texture appeared again.

Selected DSC thermograms are reproduced in *Figure 4* for the four samples and *Table 2* summarizes the detected transitions. The general behavior of the four polymers and the observed first-order transitions are in full agreement with the optical observations. However, kinetic effects are important and difficulties arised to observe the T_g values.

The PM-0,100 and PM-3,100 homopolymers show glass transitions at respectively 62 and 55°C (onset values). The T_g of PM-3,100 was easily observed during the first heating cycle, and its value is quite similar to the value obtained by Duran et al.[11] in spite of the tacticity difference. This shows that the increase of syndiotacticity in our sample is probably not important enough to increase the T_g as expected[12]. The T_g of PM-0,100 clearly appeared only after several annealings of the sample, an observation which may explain the absence of T_g observed by Duran for a similar sample.

Table 2 Phase behavior of the polymers

Samples	T_g (°C) (onset)	Phase transition (°C)
PM-0,100	62	$S_{OB} \xleftrightarrow[\text{1.2 kJ/mol}]{124} S_A \xleftrightarrow[\text{0.13 kJ/mol}]{200} N \xleftrightarrow{235} I$
PM-3,100	55	$S_{E, glass} \xleftrightarrow{55} S_E \xleftrightarrow[\text{8.5 kJ/mol}]{113} I$
PM0*		$S_{OB} \xleftrightarrow{124} S_A \xleftrightarrow{200} N \xleftrightarrow{235} I$
PM3*	55	$S_{E, glass} \xleftrightarrow{55} S_E \xleftrightarrow[\text{11.0 kJ/mol}]{113} I$
PM-0,40A	130	$K \xleftrightarrow[\text{2.6 kJ/mol}]{174} K'$
PM-0,40S		$K \xleftrightarrow[\text{20.9 kJ/mol}]{157} K'$

*Results from Refs 13 and 14.
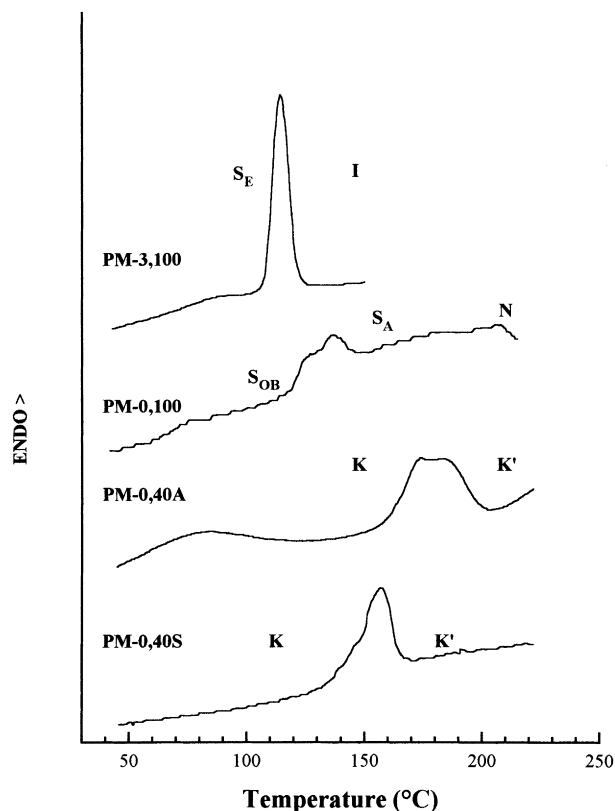
Figure 4 DSC scans of polymers. PM-0,100 (1st cycle), PM-3,100 (1st cycle), PM-0,40S (2nd or 3rd cycle) and PM-0,40A (a, 1st cycle; b, 2nd or 3rd cycle). Scans are not normalised according to the sample masses

The PM-0,40A and PM-0,40S copolymers present one single first order transition with a particularly high energy value (20.9 kJ/mol) for the syndiotactic sample—obviously caused by the full development of the crystallisation as observed under microscope and to the backbone order. The temperatures of transitions for both samples are different of 17°C, with a lower temperature for the syndiotactic sample in agreement with the results of Hann *et al.*[3].

The T_g of the atactic PM-0,40A copolymer was only clearly observed by DSC after the second heating cycle and in the absence of crystallisation (see *Figure 4*). Its much higher value (130°C) compared with that of the PM-0,100 sample is well explained by the presence of carboxylic acid units promoting strong intra- and inter-molecular interactions. No glass transition was observed for the PM-0,40S

sample even after different annealings. This is not surprising, since because of its syndiotactic structure and to the presence of the carboxylic acid groups, the T_g is expected at a high temperature, probably near the decomposition temperature.

Structural properties

X-ray diffraction experiments on the two liquid-crystalline homopolymers made possible the determination of all the mesophases involved. *Tables 3* and *4* summarize the results of the diffraction patterns in the low and wide angle region respectively.

Structural properties of PM-0,100 and PM-3,100

PM-0,100 diffraction patterns present sharp Bragg reflections at 110 and 170°C in the low angles region, corresponding to a lamellar system with stacking periods *d* comparable to the length of the monomer unit (*Table 3*). Analysis of the wide angle reflections (*Table 4*) demonstrates the presence of S_{OB} and S_A phases. In the S_{OB} phase, the packing of the pendant groups form a two-dimensional oblique lattice[13]. At 205°C, the nematic phase identified under an optical microscope is confirmed. These results are rather identical to the results obtained by Duran[13] with an analogous sample, except the identification of the nematic phase. With our sample, we observed a diffraction signal at 8.4 Å with a rather fuzzy character and the absence of Bragg diffraction at 30.0 Å. These observations contrast with the observations of Duran who observed a sharp signal at 8.4 Å and a diffuse diffraction at 30.0 Å. Considering the high viscosity of this type of sample, it is obvious that kinetic factors play an important role in the phase formation. The possible coexistence of the smectic and nematic organisations in Duran's observations may explain the observed differences.

PM-3,100 diffraction pattern presents no first order reflection in the low angle region but a very strong second order diffraction (*Table 3*). This behavior is attributed to the electronic density distribution along the normal to the layers[14]. In the wide angle region (*Table 4*), the organisation is characterized by three rather sharp Bragg reflections corresponding to spacings of 4.44 Å, 4.01 Å and 3.23 Å. This is indicative of a smectic E phase as demonstrated with similar polymers[14].

As described before, the structural parameters of PM-0,100 and PM-3,100 containing respectively 50.1% and 59.5% of syndio triads are very similar to the analogous atactic compounds with respectively 45.1% and 53.7% of

Table 3 Layer spacing d S_A, d S_{OB}, d S_E, of the smectic A, OB, E for the polymers PM-0,100 and PM-3,100 at temperature *T* upon heating and compared with lenghts D of monomeric units

Samples	T (°C)	D (Å)	d S_{OB} (Å)	d S_A (Å)	d S_E (Å)	d S_P (Å)
PM-0,100	110	16	15.8	–	–	–
PM-0,100	170	16	–	15.8	–	–
PM-0,100	205	16	–	–	–	–
PM-3,100	90 ↓	27	–	–	13	–
PM0*		16	15.8	–	–	–
PM0*		16	–	15.8	–	–
PM0*		16	–	–	–	30
						8.4
PM3*		27	–	–	26.9	–

↓ upon cooling.
*Results from Refs. [13,14].

Table 4 Wide angle Bragg reflections $d\,S_A$, $d\,S_{OB}$, $d\,S_E$, of the smectic A, OB, E for the polymers PM-0,100 and PM-3,100 at temperature T upon heating

Samples	T (°C)	$d\,S_{OB}$ (Å)	$d\,S_A$ (Å)	$d\,S_E$ (Å)	$d\,S_P$ (Å)
PM-0,100	110	4.89		–	–
		4.58			
		3.92			
	170	–	4.5	–	–
	205	–	–	–	–
PM-3,100	90 ↓	–	–	4.44	–
				4.01	
				3.23	–
PM0*		4.89	–	–	–
		4.58			
		3.92	–	–	–
		–	4.5	–	–
		–	–	–	4.7
PM3*		–	–	4.54	–
				4.01	
				3.23	

↓ upon cooling.
*Results from Refs 13 and 14.

syndiotactic triads. The increase of about 11% in syndio-tacticity is probably not important enough to modify the liquid crystalline behavior of these polymers as it can be deduced from X-ray diffraction. Although the study of polymers with higher syndio triads content would be necessary to conclude, our results are in good agreement with the general findings that the liquid-crystalline arrangements of mesogenic polymethacrylates are mainly determined by the interactions between the mesogenic groups.

Structural properties of copolymers PM-0,40S and PM-0,40A

The crystalline textures observed under optical polarized microscope for the two copolymers with atactic and syndiotactic backbones were confirmed by X-ray diffraction. In particular, PM-0,40S presents an important number of very thin Bragg reflections presenting a granular aspect characteristic of the presence of microcrystallites in the materials. Although the transition temperatures of both atactic and syndiotactic samples show a difference of 17°C, it seems reasonable to suppose that both copolymers have a similar crystal E organisation via side chain interactions as proposed by Hann et al.[3], and often observed for polymers with bulky side groups[15]. The absence of spacer in our polymers is a strong indication to presume that the backbone is more or less included in the crystals. However, when considering the easiness of crystallisation of the syndiotactic sample compared to that of the atactic sample, it is deduced that the syndiotactic arrangement of the backbone promotes the crystalline order.

Indeed, in spite of the important difference in tacticity of both copolymers, no important structural difference and no LC organisation are observed. Since a rich liquid crystalline behavior is observed with the analogous atactic homopolymer, it is obvious that the copolymeric nature of our samples is responsible for their behavior. However, experiments realized in our laboratory confirm the general observation that for methacrylate copolymers with mesogenic group contents lower than about 50%, well developed organisations are hard to observe without spacer. It is quite probable that the crystalline nature of our 40% copolymers is promoted by the alternated tendency of the grafting induced by the DCC chemical method as mentioned before. The nearly regular intercalation of the carboxylic groups between the mesogenic groups allows the backbone to adapt its configuration in order to accept the crystalline order imposed by the mesogenic groups.

CONCLUSION

In this work four polymethacrylates with different tacticity and bearing mesogenic groups have been prepared and studied in order to understand the influence of the backbone tacticity on the thermotropic properties of the polymers. It is shown that moderate variations of the syndiotactic triads content in the homopolymers do not modify the LC behavior. With carboxylic acid copolymers containing 40% of mesogenic groups without spacer, only crystalline phases are obtained for the atactic and syndiotactic structures. Such a behavior is interpreted by considering the preferential alternated structure generated by the DCC method of grafting. In this case, the syndiotactic arrangement promotes the crystalline order. All these results confirm that mesogenic interactions are the main driving force, and govern the structural behavior of such polymethacrylate polymers.

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