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Thermal properties of a series of side-chain liquid crystalline poly(methacrylates)

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Résumé. — Le comportement thermique d'une série homologue de poly(méthacrylates) liquides cristallins à groupes mésogènes latéraux a été étudié par thermogravimétrie, analyse thermique différentielle, microscopie optique en lumière polarisée et dilatométrie. L'étude menée par DSC a permis de montrer que l'équilibre n'est atteint que lentement même au-dessus de la température de transition vitreuse. Le polymorphisme thermotrope des polymères a été analysé en fonction de la longueur de l'espaceur souple. Les transitions vitreuses mises en évidence ont été discutées. La dilatométrie a permis de calculer les volumes spécifiques partiels des espaceurs souples et de montrer que, dans l'état mésomorphe vitreux, ces espaceurs sont proches de l'état cristallin ; que, dans l'état isotrope, ils sont à l'état liquide ; alors que, dans l'état mésomorphe normal, ils sont dans un état « intermédiaire » entre l'état cristallin et l'état liquide.

Abstract. — The thermal behaviour of a series of side-chain liquid crystalline poly(methacrylates) has been investigated by thermogravimetry, differential scanning calorimetry, polarizing optical microscopy, and dilatometry. The DSC study has shown that long times are required to reach equilibrium even at temperatures above the glass transition. The thermotropic polymorphism has been determined as a function of the length of the flexible spacer. Glass transitions in the mesomorphic state have been discussed. Dilatometry has shown that, for the « glassy » mesomorphic phases, the partial specific volume of the flexible spacer is close to that corresponding to the crystalline state ; that, for the normal liquid crystalline phases, it is intermediate between those corresponding to the crystal and the isotropic liquid ; and that, for the isotropic polymer, it is close to that of a liquid.
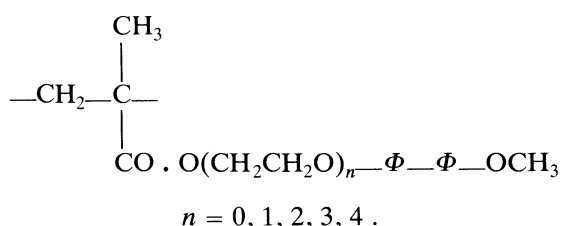
1. Introduction.

In a series of recent papers, the chemical synthesis [1], physico-chemical characterization [2], and preliminary structural studies [3-5] of certain side-chain liquid crystalline polymers were described. The polymers used were poly(acrylates) and poly(methacrylates) having 4'-methoxy-biphenylyl mesogenic pendant groups and oligo(ethylene oxide) flexible spacers. These polymers show liquid crystalline behaviour, and the general goal of this study is to understand the relationship between this behaviour and the microscopic structure of the polymers. Before complete structural work could be undertaken, however, it was important to know the thermal behaviour of the materials. This includes not only the knowledge of the transition temperatures, but also the thermal degradation behaviour, the thermal history effects on the transitions, and, of course, the thermodynamic parameters associated with the transitions.

2. Experimental.

The poly(methacrylates) used in the present work were all free-radically polymerized. Those indicated by the abbreviation PM-n have 4'-methoxy-biphenylyl mesogenic pendant groups and oligo(ethylene oxide) spacers of various lengths [1] :

$$-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CO \cdot O(CH_2CH_2O)_n-\Phi-\Phi-OCH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}-$$

$$n = 0, 1, 2, 3, 4 \ .$$

Those indicated by the abbreviation PM-m-EO have

methoxy terminated oligo(ethylene oxide) side chains attached to the polymer backbone [6] :

$$—CH_2—\underset{\underset{CO\,.\,O(CH_2CH_2O)_m—CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}— \qquad m = 3, 4\,.$$
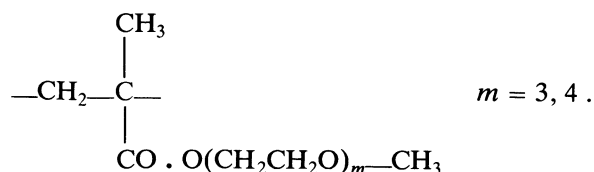
Their molecular weights and polydispersities are shown in table I. The PM-m-EO polymers are highly hygroscopic and were therefore systematically lyophilized before use.

Table I. — *Molecular weight characteristics of the polymers studied.*

Ref.	Sample	Mw ($\times 10^3$)	Mw/Mn
PM-0	RP33	22.7	3.8
PM-0	RP38	5.3	1.6
PM-1	RP23	34.7	—
PM-2	RP1	65.0	2.8
PM-3	RP6	45.9	2.7
PM-4	RP49	183.0	2.8
PM-3-EO	YF1	85.0	—
PM-4-EO	YF2	35.0	—

The experimental data on the PM-n and PM-m-EO polymers will be compared, first, to those [7] concerning a low-molecular-weight mesogenic series, abbreviated as MC-n, and used as model compounds for the PM-n monomers :

$$CH_3—\underset{\underset{CO\,.\,O(CH_2CH_2O)_n—\Phi—\Phi—OCH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}}$$

$$n = 0, 2, 3$$
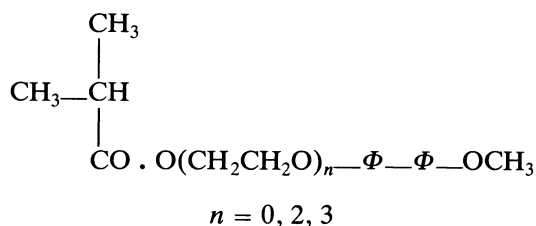
and second, to those already published in the literature [8, 9], concerning the well-known series of poly(alkylmethacrylates), abbreviated as PM-x-CH$_2$:

$$—CH_2—\underset{\underset{CO\,.\,O(CH_2)_xCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}— \qquad x = 0, 5, 7, 9\,.$$
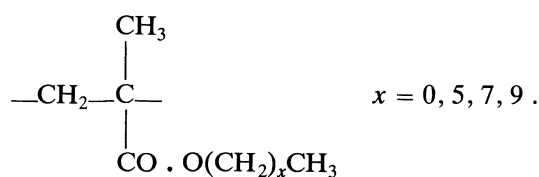
The experimental techniques utilized in this work were thermogravimetry, differential scanning calorimetry (DSC), polarizing optical microscopy, and dilatometry. Thermogravimetry was performed

on powdered samples using a Mettler TC10A instrument with a nitrogen vector gas. Dynamic measurements were made at a heating rate of 10 K min^{-1}. Static measurements were conducted at a constant temperature as a function of time. DSC studies were carried out with Perkin Elmer DSC2 and DSC4 instruments using sealed aluminum pans. Measurements were systematically made at a series of heating and cooling rates between 20 and 0.3 K min^{-1}. Optical observations were obtained with a Leitz Orthoplan polarizing microscope equipped with a Mettler FP52 hot stage.

Dilatometry was performed with a dilatometer of the classic Bekkedahl-Kovacs type which has been described elsewhere [10, 11]. Measurements were carried out using about 0.6 g of carefully degassed polymer. The absolute value of the specific volume was determined after removal of the sample from the dilatometer bulb and calibration with mercury. The temperature of the silicone oil thermostating bath was electronically controlled to within 0.01 °C. The overall precision of the measured polymer specific volume was estimated to be about 5×10^{-3} cm^3 g^{-1}. This precision is less than that usually obtained with low-molecular-weight liquid crystals for the following reasons. Complete removal of the polymer (by dissolving in a solvent and pumping the solution away through the capillary), necessary for the calibration of the dilatometer, was difficult to achieve due the high viscosity of the polymer and to its adsorption to the internal surfaces of the dilatometer. Likewise, complete degassing of the polymer was also difficult to obtain due to its high viscosity and to its incapacity for crystallization (which hindered the release of occluded gas during the freeze-thaw vacuum cycles).

3. Thermogravimetry.

Before attempting other thermal analyses and structural studies of the polymers, it was important to have an idea of their stability against thermal degradation. This was done using thermogravimetry. In the first set of experiments, the samples were heated at 10 K min^{-1} under a nitrogen atmosphere, and their weight, w, was measured as a function of the temperature, T. The onset and ending of thermal degradation, T_0, and T_1, were arbitrarily defined from the intersections with the baseline of the tangents to the peak representing the rate of weight-loss, $-\,dw/dT$, at the two inflection points. As shown in table II the thermal stability of the polymers was fairly good. The thermal degradation peaks for the PM-1 to PM-4 polymers lie at least 100 K above the clearing (liquid crystal to isotropic melt transition) temperatures discussed below.

As a second control of the stability, selected samples were held a few degrees above the clearing

Table II. — *Thermogravimetric analysis at 10 K min⁻¹ under nitrogen : T_0 is the degradation onset temperature, T_1 is the degradation termination temperature.*

Ref.	T_0 (°C)	T_1 (°C)	% weight loss
PM-0	255	480	96.93
PM-1	253	469	96.82
PM-2	257	459	96.17
PM-3	244	465	97.87
PM-4	271	457	97.26

temperature, under nitrogen, for 24 hours. For the PM-1 to PM-4 polymers, no measurable weight change occurred. For the PM-0 polymer, however, the onset of the thermal degradation peak was close to the clearing temperature, and the static thermogravimetry measurements at 220 °C showed substantial weight loss over 24 hours. As a consequence, special care was taken during the other thermal measurements of PM-0 to minimize its degradation.

4. Differential scanning calorimetry.

Side-chain liquid crystalline polymers have been described as presenting first-order transitions between mesophases and the isotropic melt, and also glass transitions frequently occurring in the temperature range of the mesomorphic phases [12]. To detect these, DSC measurements were carried out systematically on all of the PM-n and PM-m-EO polymers, and on the MC-n model compounds, from below room temperature to generally at least thirty degrees above the clearing temperature. Two points were investigated in this work. First, the thermodynamic transitions, their enthalpies, and their reversibility were studied for each sample. Second, the glass transitions and thermal history effects were analysed for the polymers. In the particular case of the PM-0 polymers, where degradation begins slightly above the clearing temperature, care was taken to avoid subjecting the samples to high temperatures over long periods of time.

A typical DSC heating and cooling scan for the PM-2 polymer is shown in figure 1. The first-order transition observed corresponds to the transition from a smectic E liquid crystalline phase, whose structure was previously studied by X-ray diffraction [4], to the isotropic melt. It is interesting to note that this transition exhibits a strong hysteresis effect, generally not seen with low-molecular-weight liquid crystals, and presumably due here to the high viscosity of the polymeric material. To better establish the kinetic origin of the supercooling effect, a number of heating and cooling scans were done at
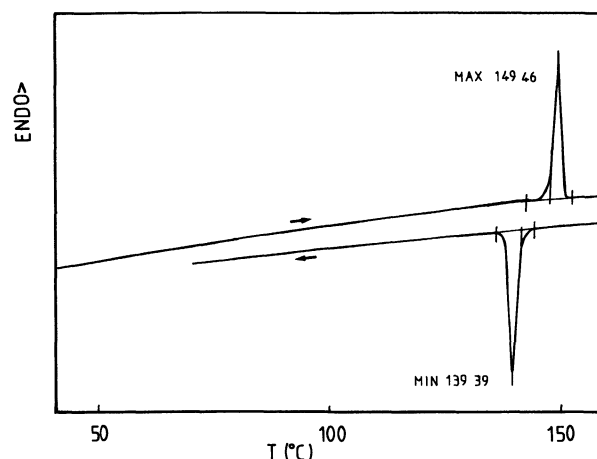

Fig. 1. — DSC heating and cooling scan of PM-2 polymer at 2.5 K min⁻¹.

various rates between 20 and 0.3 K min⁻¹. The peak onsets as a function of the scan rate for the PM-2 polymer are plotted in figure 2. It can readily be seen that the heating and cooling curves tend to the same temperature at slow rates, indicating the reversible nature of the transition. Similar experiments were done with all of the polymers ; the transition temperatures and enthalpies measured by extrapolating to zero rate, along with the corresponding calculated entropies, are shown in table III. It should be noted that the transition enthalpies of the PM-2, PM-3, and PM-4 polymers were of the same order of magnitude as the corresponding monomer model compounds (MC-2 and MC-3 which show the same mesomorphic phase [13, 7]) and significantly less than the MC-0 model compound, which transforms directly from the crystal to the isotropic liquid [7].
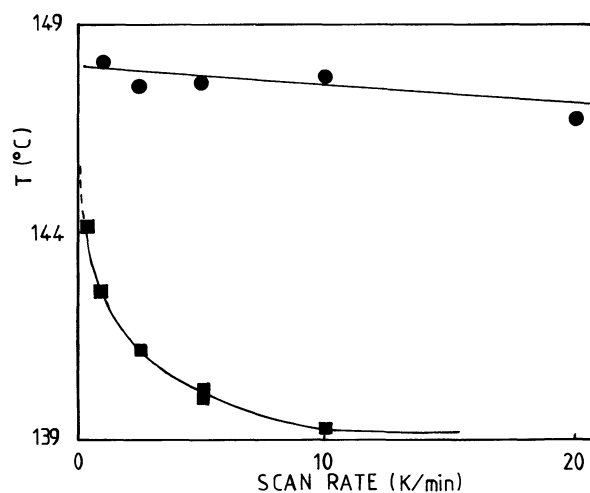

Fig. 2. — DSC peak onsets as a function of scan rate for the PM-2 polymer ; filled circles and squares indicate heating and cooling scans respectively.

Table III. — *DSC heating data for* PM-n *and* MC-n *materials : T, ΔH, and ΔS are first-order transition temperatures.*

Ref.	Sample no.	Transition Temp. (°C)	ΔH kJ mol^{-1}	ΔS J mol^{-1} K^{-1}
PM-0 (^{A})	RP33	(186)	—	—
		(201)	—	—
		(261)	—	—
PM-0	RP38	(124)	—	—
		(185)	—	—
PM-1	RP23	(120)	—	—
		137	0.88	6.3
PM-2	RP1	148	12.9	30.9
PM-3	RP6	107	11.0	29.1
PM-4	RP49	89	10.6	29.3
MC-0	RD1	128	33.3	83.1
MC-2	RD8	58	22.2	67.1
		73	13.9	40.3
MC-3 (^{B})	RD7	44	31.0	97.8
		53	15.0	46.0

(^{A}) Because of potential degradation at high temperatures, DSC results could not be extrapolated to zero rate, therefore ΔH and ΔS could not be obtained : values in parentheses are approximate.

(^{B}) Data from cooling scans.

The PM-2, PM-3, and PM-4 polymers present a single first-order transition, corresponding as mentioned above to the transition from a smectic E mesophase to the isotropic melt. No other first-order transition could be detected on cooling to or heating from $-$ 100 °C. Furthermore, it should be noted that the enthalpies and entropies measured did not change significantly depending upon the thermal history of the samples : quenching the polymers from the melt in liquid nitrogen, cooling at 0.3 K min^{-1}, or annealing just below the clearing temperature for up to two weeks.

The PM-0 and PM-1 polymers show more than one first-order transition. In contrast to the PM-2, PM-3, and PM-4 polymers, their thermotropic polymorphism depends strongly on the thermal history of the samples. Therefore, the values of the temperatures and enthalpies reported in table III for the PM-0 and PM-1 polymers are not strictly thermodynamic values corresponding to equilibrium. As will be described in a forthcoming paper, X-ray measurements have shown that the transitions observed upon heating with the PM-0 polymers correspond to the succession of a smectic OB, a smectic A, a new type of a nematic, and an isotropic phase [14]. The case of PM-1 is further discussed below.

The PM-3-EO and PM-4-EO polymers were studied in the temperature range from $-$ 100 °C to $+$ 150 °C. No evidence was seen indicating first-order transitions. This behaviour is analogous to that reported in the literature for the PM-x-CH$_2$ series with alkyl side-chains of comparable length [8].

In addition to the above study of first-order transitions, special attention was paid in the present work to detect glass transitions using DSC. The detection of glass transitions with the PM-n polymers was not very precise, as the heat capacity jump at T_g was rather weak. DSC was, nevertheless, still a convenient technique to use with the PM-n polymers, especially in conjunction with dilatometry. Values of T_g's for the PM-n and PM-m-EO polymers are found in table IV.

Table IV. — *Glass transition temperatures of liquid crystalline polymers and model compounds.*

Ref.	T_g (°C) DSC	T_g (°C) Dilatometry
PM-0-CH$_2$ (^{A})	—	104
PM-5-CH$_2$ (^{B})	—	$-$ 5
PM-7-CH$_2$ (^{B})	—	$-$ 20
PM-11-CH$_2$ (^{B})	—	$-$ 65
PM-3-EO	$-$ 52	—
PM-4-EO	$-$ 55	—
PM-1	—	84
PM-2	99	94
PM-3	55	49
PM-4	37	38

(^{A}) Data from atactic PMMA, reference [9].
(^{B}) Data from reference [8].

DSC also proved useful for studying the special case of the « glass transition » reported in the literature for PM-1 [15]. Some selected scans obtained in this work are shown in figure 3. Curve 1 corresponds to the heating trace at 20 K min^{-1} and compares well to what has already been found and interpreted as a glass transition (see curve I-M, Fig. 3, Ref. [15]). Curves 2, 3, and 4 correspond to the heating traces registered at 10 K min^{-1} with samples which had been annealed at 100 °C for various times. With no annealing (curve 2), one again finds what appears to be a glass transition. After annealing for three days (curve 3), the « glass transition » has turned to a weak first-order transition ; after annealing for one week (curve 4), this first-order transition has become quite important. The same conclusion may be drawn from the cooling scan at 2.5 K min^{-1} (curve 5). It seems, therefore, that the « glass transition » is actually a kinetically hidden first-order transition which is revealed either by annealing or on cooling at low rates. Figure 4 shows how the enthalpy associated with this transition develops on decreasing the cooling rate, as
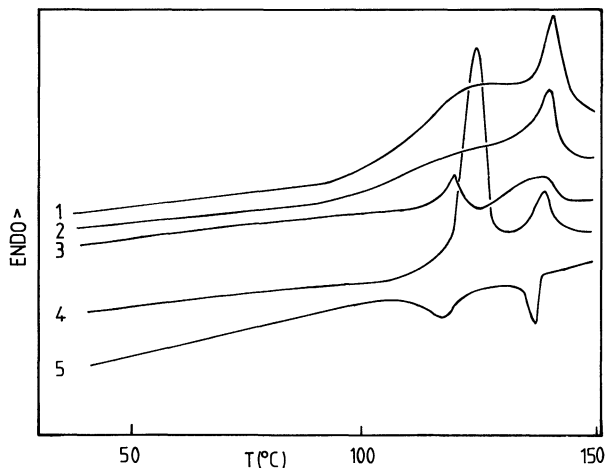
Fig. 3. — Selected DSC scans of PM-1 (RP23) polymer ; curve 1, heating scan at 20 K min^{-1} ; curve 2, heating scan at 10 K min^{-1} with no annealing ; curve 3, heating scan at 10 K min^{-1} after annealing at 100 °C for 3 days ; curve 4, heating scan at 10 K min^{-1} after annealing at 100 °C for 7 days ; curve 5, cooling scan at 2.5 K min^{-1}.
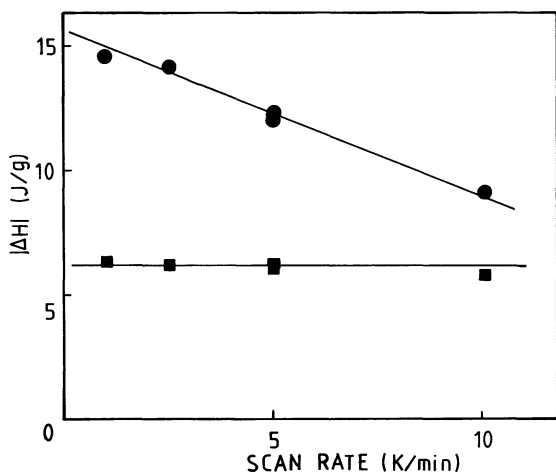

Fig. 4. — Transition enthalpies for PM-1 (RP23) as a function of the cooling rate ; filled squares correspond to the 120 °C peak, for the « glass transition » ; filled circles correspond to the 137 °C peak, for the liquid crystal-isotropic melt transition.

compared with the enthalpy of the transition from the liquid crystal to the isotropic melt, which is independent of the cooling rate. The appearance also of crystallization on annealing [16] has been seen with other side-chain liquid crystalline polymers and was attributed to a metastable liquid crystalline phase. This thermal history dependence indicates the importance of careful thermal studies in characterizing the phase behaviour of these polymers.

5. Optical microscopy.

Optical microscopy is a classical technique to identify liquid crystalline phases in low-molecular-weight

organic compounds. It is also currently used with success in the field of polymeric liquid crystals. Observations of the PM-2, PM-3, and PM-4 polymers as a function of the temperature were straightforward. The textures obtained on annealing for several days just below the clearing temperatures (Fig. 5) clearly indicated the presence of an ordered smectic phase. X-ray studies [4] confirmed the existence of a smectic E phase.
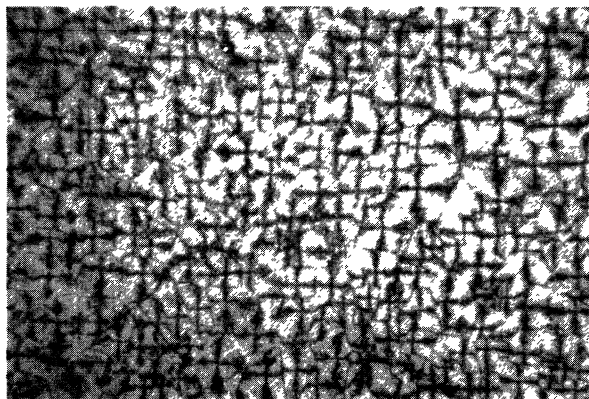

Fig. 5. — Optical micrograph of PM-2 polymer at 100 °C under crossed polars.

The optical study of the PM-0 polymer, which presented three first-order transitions by DSC, was more complicated to perform. The polymer referenced RP33 (see Tab. I) had the highest molecular weight between the two PM-0 polymers considered in the present work. On cooling from the melt, this polymer showed birefringent droplets which further developed into a typical schlieren texture with two- and four-brush point singularities. This texture is typical of a nematic phase. The structure, however, corresponds to the stacking of « palissades » of ribbons [5], and the relationship between the texture observed and the structure established is discussed elsewhere [14].

At lower temperatures, the textures changed very slowly, but not in an informative way. The polymer referenced RP38 (see Tab. I) had a substantially lower molecular weight and lower transition temperatures (see Tab. III), but gave the same order of phases as RP33, as shown by X-ray diffraction [14]. It was much easier to study with optical microscopy, owing to its lower viscosity and hence to characteristic textures which developed more quickly. On cooling at a rate lower than 1 K min^{-1}, this polymer also showed birefringent droplets which again developed into a typical schlieren texture (Fig. 6a). Then, on further cooling, a gradual change of texture occurred over a rather wide temperature range, leading to the formation of a fan texture at about 185 °C (Fig. 6b, c, d). This texture corresponds to a
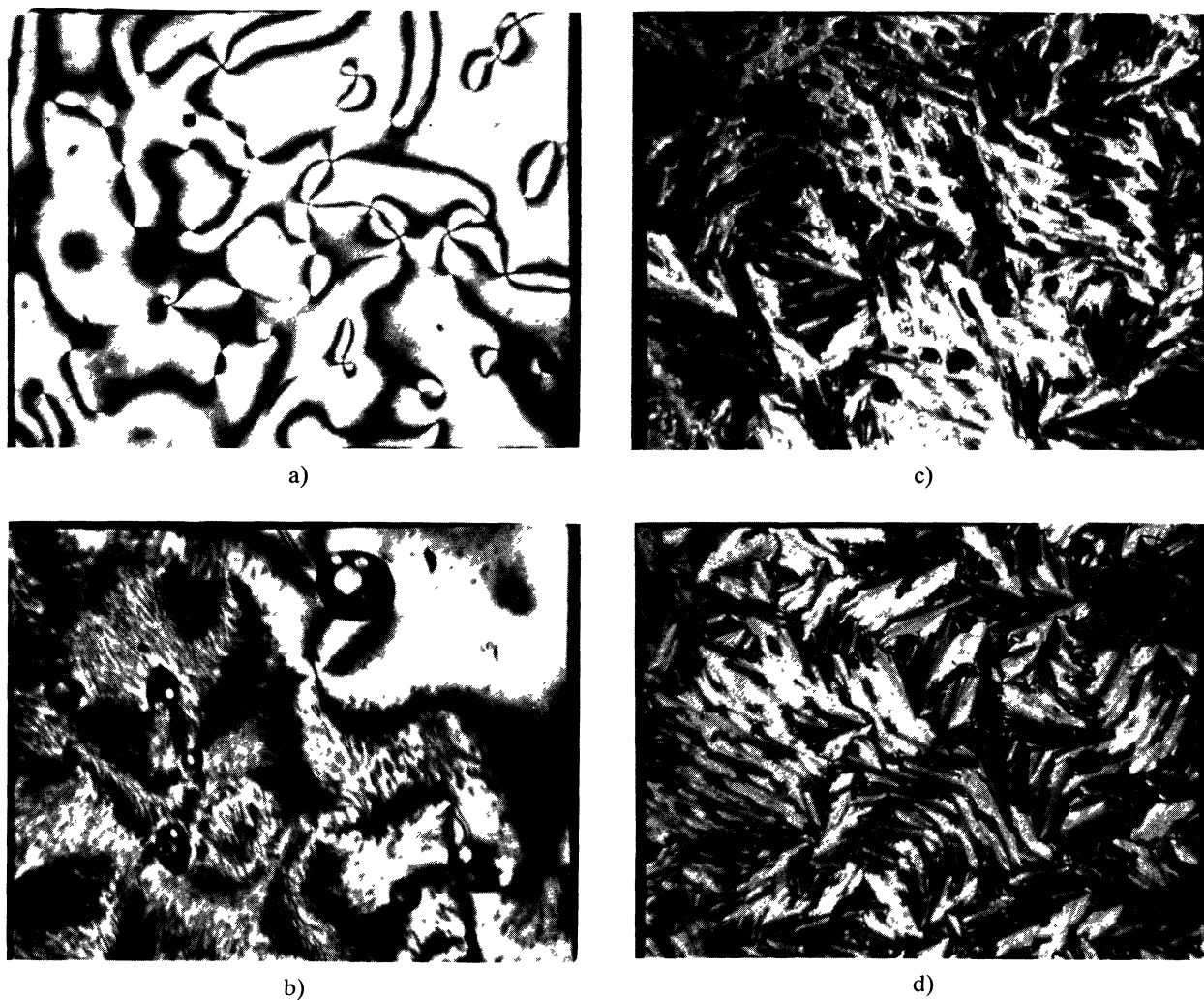
a)

c)

b)

d)

Fig. 6. — Optical micrographs of PM-0 (RP38) polymer under crossed polars ; a) 216 °C ; b) 192 °C ; c) 188 °C ; d) 180 °C.

smectic A phase as confirmed by X-ray diffraction [14]. Finally, at much lower temperatures, below the transition at 124 °C detected by DSC, the textures did not show any significant change.

As for the PM-1 polymer, its behaviour under the microscope was very similar to what was seen for the PM-0 polymer referenced RP33 described above. On cooling below the melting temperature at 138 °C, and annealing for a long time, a schlieren texture was developed which did not change on further cooling.

The transition temperatures observed by microscopy for the PM-n polymers, reported in table V, are in agreement with those measured by DSC.

6. Dilatometry.

Dilatometry was performed on the PM-1, PM-2, PM-3, and PM-4 polymers. Due to the thermal stability problems pointed out in the thermal gravimetry section above, degassing of the PM-0 polymer turned out to be impractical, thus prevent-

Table V. — Transitions obtained from optical microscopy.

Ref.	Sample no.	T_2 (°C)	T_3 (°C)
PM-0	RP33	—	265
PM-0	RP38	185	230
PM-1	RP23	—	138
PM-2	RP1	—	150
PM-3	RP6	—	105
PM-4	RP49	—	90

ing dilatometry on this polymer. Measurements of the absolute value of the polymer specific volume, $\bar{v}$, were made by several static heating and cooling scans, that is temperature steps of 1 °C followed by 15 min of thermal equilibration.

The PM-2, PM-3, and PM-4 polymers showed reproducible and smooth volume curves within the

temperature range of thermal stability of each phase, independent of the thermal history of the samples. A typical heating and cooling scan for the PM-3 polymer is plotted in figure 7. This shows the excellent agreement of the specific volumes measured on heating and cooling (though occasionally on cooling, the volume decreased stepwise due to the sticking of the polymer on the vessel walls). Figure 7 also shows the supercooling effect seen above by DSC for the transition from the liquid crystal to the isotropic melt. Following the criteria generally used in polymer science, the change in slope at 49 °C indicates a glass transition [12]. It is worth noting that, within the existence domain of the « glassy » smectic E, the normal smectic E, and the isotropic liquid, the specific volumes vary linearly with temperature, allowing calculation of thermal expansion coefficients :

$$\alpha = (1/\bar{v}) \, (d\bar{v}/dT) \, .$$

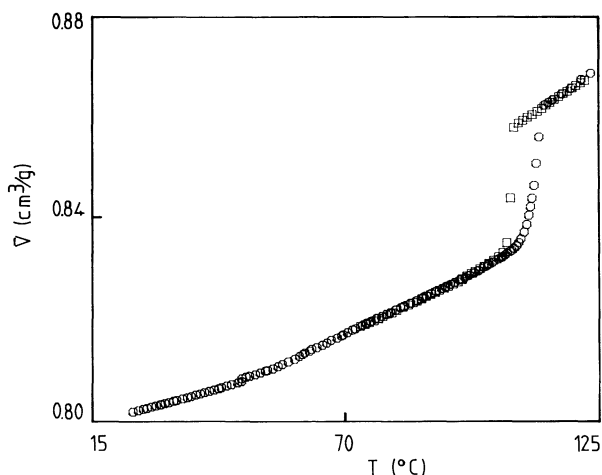Table VI shows the thermal parameters determined experimentally.

Fig. 7. — Dilatometry heating and cooling trace of PM-3 polymer, specific volume as a function of temperature ; open circles correspond to the heating trace, open squares correspond to the cooling trace.

From the experimental data, and by assuming the additivity of the partial molar volumes of the polymer backbone, the spacer, and the mesogenic group in the polymer, it is possible to calculate the partial molar volume of the spacer alone at a given temperature and for a given thermodynamic phase. Indeed, as stated above, the PM-2, PM-3, and PM-4 polymers all exhibit the same « glassy » smectic E, normal smectic E, and isotropic phases. Then the difference in their molar volumes per repeat monomer unit corresponds to the partial molar volume of an ethylene oxide, CH_2CH_2O, monomer unit in the spacer at a given temperature (Tab. VII).

The PM-1 polymer was complicated to study by dilatometry, as well as by DSC. The volume scans as a function of temperature, in the range below the clearing temperature, were not reproducible, depending strongly upon the thermal history of the sample. The values reported in table VI for PM-1, therefore, are only approximate.

Table VII. — *Specific volume of ethylene oxide spacer in smectic* E *phase of* PM-2, PM-3 *and* PM-4 *polymers.*

Temp. °C	ΔV per EO	$\bar{v}_{EO}^{calc}$	$\bar{v}_{EO}^{crys}$	$\bar{v}_{EO}^{liq}$
25	36.0 ± 1	0.82_4	0.815	0.891
87	39.6 ± 2	0.87_6	0.824	0.930
130	41.6 ± 1	0.94_5 ([A])	0.831	0.956

([A]) For PM-2, $\bar{v}$ values extrapolated from the isotropic part of the curve.

7. Discussion.

The glass transition temperatures determined by dilatometry and DSC are compared in table IV with those of selected polymeric model compounds : PM-m-EO and PM-x-CH$_2$ (Tab. I). Two trends in the glass transition are observed. The first is a decrease of the polymer T_g for each series as the spacer length

Table VI. — *Dilatometry data for* PM-n *polymers.*

Ref.	α_g	α_1	T_1	α_2	T_2	α_{Liq}	$\Delta \bar{v}_{T_1}$
PM-1	2.03	4.85	(128) ([A])	8.83	(140) ([A])	6.58	—
PM-2	2.32	4.96	151	—	—	6.55	3.62
PM-3	2.96	5.19	108	—	—	6.44	2.65
PM-4	3.18	5.43	92	—	—	6.51	2.0
PM-0-CH$_2$ ([B])	2.99	—	—	—	—	5.79	—

([A]) Values in parenthesis are approximate.
([B]) Data for atactic PMMA from reference [9].

increases, compatible with a classical plasticization effect. The second is a substantial (about 100 °C) shift to higher temperatures of the PM-n polymer T_g's compared to those of the corresponding model compounds ; this « rigidification » effect induced by the mesogenic biphenyl groups — which is compatible with the ordering of the polymer backbone observed by ^{2}H NMR [17] — indicates that the decoupling of the backbone from the mesogenic groups through the spacers is not as efficient as generally assumed [12].

This poor decoupling of the mesogenic group from the polymer backbone is also illustrated by the first-order transition temperatures included in table III. Indeed, it is interesting to note that the thermal stability of the mesomorphic phases of the PM-n polymers is significantly higher than that of the same mesomorphic phases of the corresponding monomer model compounds MC-n. It is also worth mentioning that, in the absence of any spacer, the monomer model compound MC-0 does not produce liquid crystals, whereas the polymer PM-0 shows three mesomorphic phases with a clearing temperature more than 100 °C higher than the melting temperature of MC-0. Instead of being neutral when separated from the mesogenic groups by long spacers, or disturbing the mesomorphic behaviour in the absence of a spacer, the polymer backbone plays, therefore, an active rôle in « enhancing » the mesomorphic character and « stabilizing » the mesomorphic phases in these polymers.

The observed jumps of the molar enthalpy, entropy (Tab. III), and volume (Tab. VI) per monomer repeat unit at the transition from the smectic E mesophase (PM-2, PM-3, and PM-4) to the isotropic liquid do not increase with the spacer length. As will be seen below, this is due to the fact that the spacer is already substantially disordered in the mesomorphic state and does not measurably participate in the melting process.

The cubic thermal expansion coefficients of the PM-n polymers are compared with those of PM-0-CH$_2$ (PMMA) in table VI. The α values of the « mesomorphic glass » and the isotropic liquid phases of PM-n are similar to those for PMMA in the glassy and liquid states. In general, the mesomorphic phases have values intermediate between the glass and the melt. For the PM-1 polymer in the high temperature mesomorphic state, however, α is higher than in the melt, as observed with nematic liquid crystals [18].

The calculated partial molar volumes per ethylene oxide monomer unit in the spacer for the PM-n polymers are compared in table VII with those calculated for the crystalline and liquid poly(ethylene oxide) homopolymer. For the latter, values were obtained using corresponding published data for the specific volumes ($\bar{v}_{cr} = 0.8152$ and $\bar{v}_{liq} = 0.8907$ cm^3 g^{-1} at 25 °C) [19] and for the cubic thermal expansion coefficients ($d\bar{v}/dT = 1.5 \times 10^{-4}$ and 6.9×10^{-4} cm^3 g^{-1} K^{-1} for the crystal and liquid respectively) [20]. It is of particular interest to note that, within the precision of the experiment, the spacer seems to be in the liquid state in the isotropic liquid phases, close to the crystal in the « glassy » smectic E phases, and in an « intermediate state » between the crystal and the liquid in the normal smectic E mesophases. The conclusion that the spacer in the normal smectic E phase is in an « intermediate state » between the crystal and the isotropic liquid seems in contradiction with ^{2}H NMR observations [17] showing that the order parameter in the spacer is lower for the polymer mesophase than for the corresponding monomeric model compound. However, this contradiction is only apparent, since dilatometry measures compactness while NMR provides an estimate of the orientational order parameter of chemical bonds in the spacer.

With soaps [21] and low-molecular-weight rod-like organic mesogens [22], the occurrence of liquid crystals upon heating was connected with intramolecular melting of the flexible aliphatic parts of the molecules. With side-chain liquid crystalline polymers the flexible spacers are not completely molten, but in an « intermediate state ». This is easy to understand since, for side-chain polymers, the flexible spacers are constrained at both of their ends, one being attached to the polymer backbone, the other to the pendant mesogenic group. Conversely, for classical low-molecular-weight liquid crystals, the flexible chain is constrained at only one end and free at the other.

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