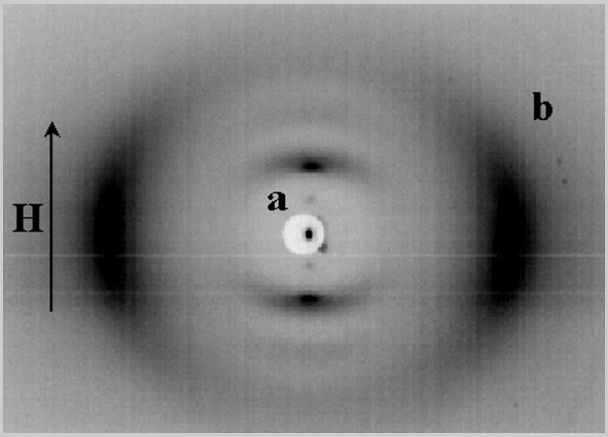
Full Paper: Side-on and side-end liquid-crystalline (LC) polymethacrylates were synthesized by atom-transfer radical polymerization at 20 °C using monofunctional and difunctional initiators. The polymers have narrow molecular-weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.15–1.45). The polymerization kinetics were determined for a side-on LC methacrylate, and appear to be first-order, whatever the initiator used. However, the measured molecular weight is much larger than expected, probably because the initiation step is slow. The thermotropic properties of the LC polymers were studied by thermal optical polarizing microscopy, differential scanning calorimetry, and X-ray diffraction. For a side-end LC polymethacrylate, two LC phases were detected although only one has been reported in the literature. The phase sequence was shown to be Cr–SmA–N–Iso.



X-ray diffraction pattern of **P4** in the smectic A phase (T = 120 °C) (a) small-angle Bragg reflections; (b) wide-angle reflection. **H** is the direction of the applied magnetic field.

Liquid-Crystalline Polymethacrylates by Atom-Transfer Radical Polymerization at Ambient Temperature

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Introduction

To properly investigate the structure/property relationships of liquid-crystalline (LC) polymers, it is important to have samples of narrow molecular-weight distribution ($\overline{M}_w/\overline{M}_n < 1.3$). This becomes a crucial issue when the LC polymer is a part of LC/Iso or LC/LC block copolymers (Iso: isotropic), because only block copolymers with a narrow molecular-weight distribution of each of their components display very regular, long-range ordered structures. Block copolymers containing LC block(s) are fascinating self-assembling systems; several reviews on this subject have appeared recently.[1–4] One of the challenges in this field is to synthesize all the structural variations possible with well-defined molecular structures.

The most suitable method to synthesize LC side-chain (co)polymers with a narrow molecular-weight distribution is a "living" polymerization. LC monomers have been polymerized in a "living" manner by anionic, cationic, ring-opening metathesis, or group transfer polymerization techniques.[1–3] Recently, controlled ("living") radical polymerizations e.g., nitroxide-mediated radical polymerization[5,6] and atom-transfer radical polymerization (ATRP),[7] have also been used to synthesize LC side chain (co)polymers. Compared with the methods mentioned above, these controlled radical polymerizations have some benefits: the number of monomers that can be (co)polymerized is quite extensive, and the reactions are not water-sensitive and do not require ultrapure solvents and reagents. ATRP is of particular interest, since it is applicable to both styrenic and (meth)acrylate monomers and is remarkably tolerant of functional groups. To our

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knowledge, the only LC polymer prepared so far by ATRP is a side-chain (side-end-type) polyacrylate.[7]

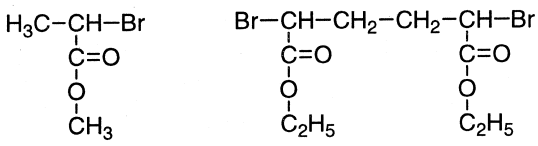
In this paper, we report the synthesis of some side-on and side-end LC polymethacrylates via ATRP at ambient temperature. Polymers with narrow molecular-weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.15–1.45) and rather high molecular weights were obtained. The ATRP kinetics of a side-on LC methacrylate monomer were studied in detail at 20 °C, using either a monofunctional or a difunctional initiator. The thermotropic properties of the LC polymers were studied and compared with those of polymers synthesized by conventional radical polymerization.

Experimental Part

We followed the method of Matyjaszewski[8] for ATRP synthesis. The transition-metal catalyst was Cu^IBr and the ligand was 4,4′-di(nonyl)-2,2′-bipyridine (bpy9). Alkyl bromides (Figure 1) were used as initiators. The monomers are listed in Figure 2. Their syntheses are described elsewhere.[9, 10] Cu^IBr (98%, Aldrich) was purified before use as previously described.[11, 12] bpy9 was synthesized according to reported procedures.[12, 13] The monofunctional initiator **I1**, methyl 2-bromoproprionate (98%, Aldrich), and the difunctional initiator **I2**, diethyl *meso*-2,5-dibromoadipate (98%, Acros), were used without further purification.

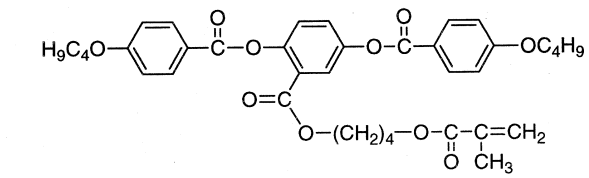
A typical ATRP synthesis was performed as follows. Cu^IBr (2.79 mg, 0.0194 mmol), initiator **I2** (3.50 mg, 0.00972 mmol), bpy9 (15.86 mg, 0.0389 mmol) and monomer **M1** (0.629 g, 0.974 mmol) ($[Cu^IBr]/[bpy9]/[\mathbf{I2}]/[M]_0$ = 2/4/1/100) were added into a Schlenk-type flask. The flask was degassed by 4 vacuum–argon cycles. Benzene (1.5 mL), which was previously degassed by bubbling argon for 30 min, was then introduced into the flask using a syringe purged with argon. With the progressive solubilization of Cu^IBr, the solution became dark brown (10–20 min). The reaction solution was stirred at room temperature (20 °C) for 21 h. The resulting polymer solution was poured into a large volume of diethyl ether. The precipitated polymer **P1** was purified twice by dissolution in a small amount of toluene and precipitation into a large volume of diethyl ether. The white polymer was dried under vacuum at 50 °C for 3 d.

Initiator **I1** (in liquid state) was used in solution in benzene: it was added into the flask after the degassing cycles and before the addition of benzene. We kept the same monomer-to-initiator ratio as for **I2**, while the ratios of Cu^IBr to initiator and of bpy9 to initiator were divided by 2, i.e., $[Cu^IBr]/[bpy9]/[\mathbf{I2}]/[M]_0$ = 1/2/1/100.

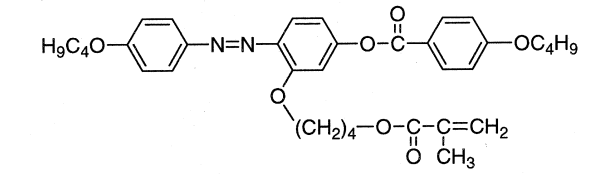


I1 **I2**

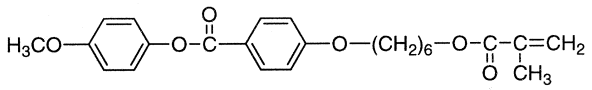
Figure 1. Monofunctional and difunctional initiators.



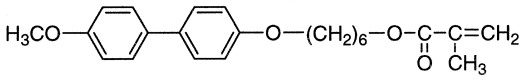
M1



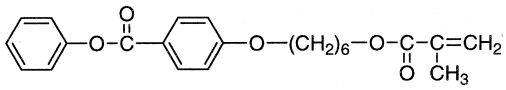
M2



M3



M4



M5

Figure 2. Monomers used in this paper.

For kinetic studies, larger amounts (4 times the above quantities) of reactants were used, while keeping the same catalyst/initiator/monomer ratios, and aliquots were withdrawn periodically from the flask using a syringe for the determination of the conversion and the molecular weight. Conversion was measured by gravimetry.

Conventional radical polymerizations were conducted as described previously.[9]

The molecular weights and the molecular-weight distributions were measured by size exclusion chromatography (SEC) using Waters Styragel™ HR 5E columns and a Waters™ 410 differential refractometer, on-line with a Wyatt miniDAWN light-scattering instrument. Tetrahydrofuran was used as the eluent at 1 ml · min^{-1}. The differential refractive index d*n*/d*c* was measured separately on the same refractometer: we found 0.156 $cm^3 \cdot g^{-1}$ for **P1** and 0.193 $cm^3 \cdot g^{-1}$ for **P2**. The mesomorphic properties were studied by thermal optical polarizing microscopy, differential scanning calorimetry (DSC), and X-ray diffraction. For microscopic observation, we used a Leitz Ortholux equipped with a Mettler FP82 hot stage and for the calorimetric study, a Perkin-Elmer DSC7. The X-ray scattering experiments

Table 1. LC polymethacrylates obtained by ATRP in benzene at 20 °C. [Cu^{I}Br]/[bpy9]/[**I1**]/[M]$_0$ = 1/2/1/100, [Cu^{I}Br]/[bpy9]/[**I2**]/[M]$_0$ = 2/4/1/100, [M]$_0$ = 0.47 M ([M]$_0$: initial monomer concentration).

Polymer	Monomer	Initiator	Time / h	Conversion	$\overline{M}_{n,Meas}$ / Dalton	DP$_{n,Meas}$ [a]	$\overline{M}_w/\overline{M}_n$	$\overline{M}_{n,Calc}$ [b] / Dalton	$\overline{M}_{n,Calc}/\overline{M}_{n,Meas}$
P1-1	**M1**	**I2**	21.25	84.6%	89410	138	1.21	55010	0.62
P1-2	**M1**	**I1**	46	72.7%	107100	165	1.23	47130	0.44
P2-1	**M2**	**I2**	21.25	43.6%	68440	114	1.17	25730	0.39
P2-2	**M2**	**I2**	49	89.6%	90930	151	1.23	53170	0.58
P3	**M3**	**I2**	21.25	76.9%	69190	113	1.40	32040	0.46
P4	**M4** [c]	**I2**	21.25	75.9%	56560	154	1.45	29970	0.53
P5	**M5**	**I2**	21.25	75.2%	61180	161	1.45	29010	0.47

[a] DP is the degree of polymerization.
[b] $\overline{M}_{n,Cal} = MW_M \times ([M]_0/[\mathbf{I}]) \times$ Conversion + $MW_\mathbf{I}$, where MW_M is the molecular weight of the monomer and $MW_\mathbf{I}$ that of the initiator.
[c] Conditions: [**M4**] = 0.53 M, [**I2**]/[**M4**] = 1/106.

were performed on a sample contained in a glass capillary tube (1-mm diameter) using CuK$_\alpha$ radiation (λ = 1.54 Å) from a 15-kW anode generator. The sample was aligned in situ in the oven of the X-ray set up by a magnetic field of 1.7 Tesla. The alignment was obtained by cooling slowly (0.2 °C · min^{-1}) the sample in the magnetic field from the isotropic phase to the given temperature of the LC phase. The scattered X-rays were detected on image plates. The instrumental resolution was limited by the size of the beam (around 0.5 × 0.5 mm^2).

Results and Discussion

Polymerization Results and Kinetic Studies

Table 1 summarizes the synthesis conditions and the characteristics of different polymethacrylates obtained by ATRP. All polymers have a narrow molecular-weight distribution: $\overline{M}_w/\overline{M}_n$ = 1.23 for the two side-on polymers, $\overline{M}_w/\overline{M}_n$ = 1.40–1.45 for the three side-end polymers. Using **I2** as the initiator, 75–85% conversion was reached after about 21 h of polymerization at room temperature for all monomers, **M2** excepted, for which a conversion of only 43.6% was once attained.[b]

The ATRP method we used appears robust and tolerates well the functional groups, ether (—O—), ester (—O—(C═O)—) and azo (—N═N—), present in our monomers. The number of ether and ester groups seems to have no influence on the results. However, the measured molecular weights $\overline{M}_{n,Meas}$ of all polymers are larger than $\overline{M}_{n,Calc}$ expected ($\overline{M}_{n,Calc} = MW_M \times ([M]_0/[\mathbf{I}]) \times$ Conversion + $MW_\mathbf{I}$, where MW_M is the molecular weight of the monomer and $MW_\mathbf{I}$, that of the initiator.)

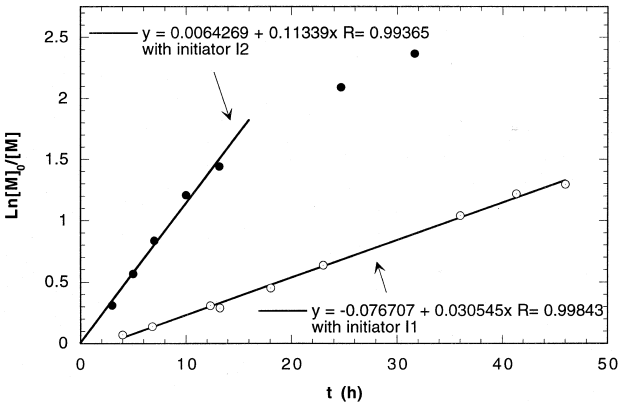


Figure 3. Kinetic plot for the ATRP of **M1** at 20 °C in benzene solution using either **I1** (open circles) or **I2** (filled circles) as the initiator. The concentrations are: [M]$_0$ = 0.47 M, [Cu^{I}Br]/[bpy9]/[**I1**]/[M]$_0$ = 1/2/1/100 when using **I1** and [M]$_0$ = 0.47 M, [Cu^{I}Br]/[bpy9]/[**I2**]/[M]$_0$ = 2/4/1/100 when using **I2**.

In order to gain some information on the polymerization mechanism of the LC methacrylates described above, we determined the ATRP kinetics of **M1**, using either **I1** or **I2** as initiator. Figure 3 shows the conventional kinetic plots for the ATRP of **M1** initiated by **I1** and **I2**. We observe a linear increase of ln[M]$_0$/[M] with time in two cases, although some deviation (slowing down of the reaction rate) might come into play above 75% conversion. This shows that the ATRP of **M1** is first-order and that the number of growing chains remains constant, at low percentage conversions. From the slope of ln[M]$_0$/[M] vs. time, the apparent propagation rate constants can be obtained: we found $k_{app,\mathbf{I1}} = 8.48 \times 10^{-6}$ s^{-1} for the polymerization initiated by **I1**, while $k_{app,\mathbf{I2}} = 3.15 \times 10^{-5}$ s^{-1} for the polymerization initiated by **I2**. Thus, we have: $k_{app,\mathbf{I2}} \approx 4 \times k_{app,\mathbf{I1}}$. Assuming the following scheme for the polymerization:[15]

[b] The main difference between **M2** and the other monomers is the presence in the structure of an azo group. In a recent study of chain transfer to polymer in radical polymerization of mesogenic acrylates,[14] it was reported that azobenzenes have higher chain-transfer constants compared to biphenyl and phenyl benzoates. However, this explanation is not fully satisfactory since, in our case, the molecular-weight distribution remains as narrow as for the other monomers (see Table 1).

$$C{-}Br + Cu^{I}Br \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P^{\bullet} + Cu^{I}Br_2 \quad (1)$$

$$P^{\bullet} + M \xrightarrow{k_p} PM^{\bullet} \quad (2)$$

the polymerization rate can be written as:

$$-\frac{d[M]}{dt} = k_{app}[M] = k_p[M][P^{\bullet}] \quad (3)$$

where $[P^{\bullet}]$ is the concentration of propagating chains and C—Br refers to the initiation site:

$$[C{-}Br]_{I2} = 2\,[C{-}Br]_{I1}$$

Under steady-state conditions, $[P^{\bullet}]$ remains constant and is equal to:

$$[P^{\bullet}] = \frac{k_{act}[C{-}Br][Cu^{I}Br]}{k_{deact}[Cu^{II}Br_2]} \quad (4)$$

Thus, if the concentration of $Cu^{II}Br_2$ in the reaction flask is the same for the polymerization initiated by **I2** as for that initiated by **I1**, despite the doubling of $[Cu^{I}Br]$, the rate of polymerization should be multiplied by a factor of 4. This is indeed what is observed. The same result was reported by Moineau et al.[16] for the ATRP of butyl acrylate at 85 °C in toluene. They used the same initiators as in this paper but the catalyst was a Ni^{II}/Ni^{III} based system. Haddleton et al. found, however, that the methyl methacrylate polymerization rate was only doubled when a difunctional instead of a monofunctional initiator (of similar chemical structure) was used.[17] In their case, the catalyst was the same as in this paper, although the ligand was different, the temperature was higher and the solvent was xylene. They argued that $[Cu^{II}Br_2]$ increased in the same manner as $[Cu^{I}Br]$ and therefore the polymerization rate was only multiplied by 2 as a result of the doubling of initiator sites. Our ATRP was conducted at 20 °C, a temperature at which the solubility of Cu^{II} species could be low. Perhaps the concentration of $Cu^{II}Br_2$ was limited by its solubility and its concentration would therefore be the same when using either **I2** or **I1**, despite the doubling of $[Cu^{I}Br]$. As a result, we found a factor of 4 for the polymerization rate constant. Further investigation is needed to elucidate this point. Nevertheless, it can be concluded from the kinetic studies that the difunctional initiator **I2** has 2 initiation sites that display efficiencies similar to the initiation site of the monofunctional molecule **I1**. This is an important result for the preparation of LC/Iso block copolymers.

In Figure 4, the measured average molecular weight $\overline{M}_{n,Meas}$ is reported versus conversion for the polymerization of **M1** initiated by **I1**. A similar curve was obtained for **M1** initiated by **I2**. We remind the reader that these data were obtained by light scattering and are therefore absolute values. If a conventional calibration method had been used, a large error in the determination of $\overline{M}_n$ would have been made, because the molecular weight of the monomer is very high (typically 400–600 g · mol^{-1}) and the chemical structure of the polymer is very different compared to those of usual narrow-molecular-weight standards. It can be noticed that $\overline{M}_{n,Meas}$ increases linearly with conversion. However, the intercept at zero conversion is quite high, at about 50% of the molecular weight at the end of the reaction. Correlatively, the measured molecular weight of the polymers is much larger than expected. Nevertheless, the polydispersity index remains low over the whole range of conversion as shown in Figure 5.

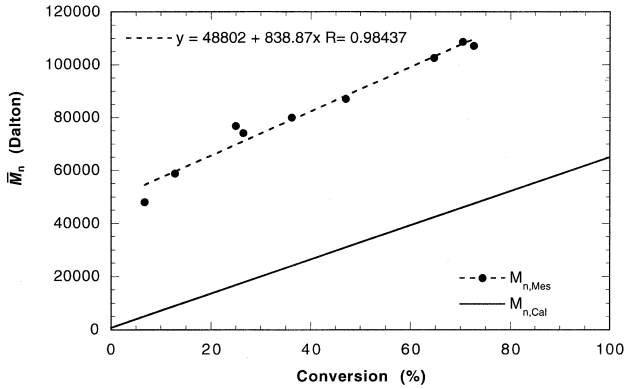


Figure 4. Dependence of measured molecular weight, $\overline{M}_{n,Meas}$, on monomer conversion for the ATRP of **M1** at 20 °C in benzene solution using **I1** as the initiator. The conditions are the same as for Figure 3.

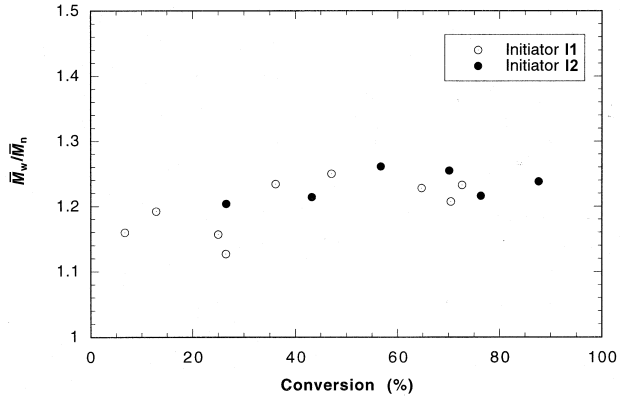


Figure 5. Dependence of polydispersity, $\overline{M}_w/\overline{M}_n$, on monomer conversion for the ATRP of **M1** at 20 °C in benzene solution with either **I1** (open circles) or **I2** (filled circles) as the initiator. The conditions are the same as for Figure 3.

At the present time, it is difficult to give explanations that would account for all these results. It is however likely that the initiation step is relatively slow compared to the propagation. This can be indirectly noticed on the SEC chromatograms shown in Figure 6: relatively low-molecular-weight chains are still present even after 70% conversion, yielding an increasingly asymmetrical chromatogram shape. This is not reflected in an increase of the polydispersity index because this parameter is too coarse being an average, nor does it affect the polymerization rate, which remains compatible with simple first-

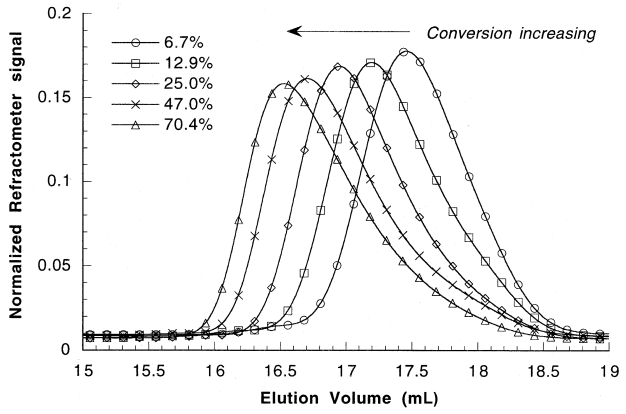


Figure 6. SEC chromatograms for the ATRP of **M1** at different conversions (6.7%, 12.9%, 25.0%, 47.0%, 70.4%). The polymerization was initiated by **I1** at room temperature under the same conditions as for Figure 3. The refractometer signals were normalized to the injected sample weight.

order kinetics over the whole range of conversion. The polymerization rate depends strongly on the concentration of the Cu^{II} species, which is relatively low when initiation is slow. Similar observations were made with some initiation systems used in the ATRP of methyl methacrylate.[18] This slow initiation could be responsible for the high molecular weight at low conversion because the concentration of Cu^{II} is too small to ensure an efficient deactivation of the first growing chains. A portion of these first growing chains would terminate as in a conventional radical polymerization. They are then dead chains, which remain as the low molecular part and lead to the asymmetrical SEC chromatogram at high conversion. The reason for this small initiation rate is probably related to the reaction temperature (kept at 20 °C) and also to the monomer concentration, which is intrinsically limited because of the high molecular weight of the solid LC monomers. By comparison, ATRP of "classical" methacrylates (or acrylates) are conducted at higher temperature (typically 90 °C) and at a monomer concentration typically one order of magnitude greater than in this study ($[M]_0 = 0.47$ M). To accelerate the initiation step, temperature could be increased in conjunction with the addition of Cu^{II} to keep the number of active chains very low and to keep the polymerization under control. Other initiators could also be tried, such as ethyl 2-bromoisobutyrate, which has a structure similar to the methacrylates, or arenesulfonyl chlorides, which were found to be efficient for methacrylate polymerization.[12]

Thus, it appears that LC methacrylates can be polymerized by ATRP under mild conditions: room temperature (20 °C) and rather low concentration ($[M]_0 = 0.47$ M). The reason for this easy polymerization is not yet understood. To our knowledge, there are very few examples in the literature of similar successful ATRPs at room temperature. Haddleton et al. described the bulk polymerization of methyl methacrylate ($[M]_0 = 9.36$ M) at 25 °C with 92% conversion after 20 h of reaction.[19] Xia and coworkers reported the rapid bulk polymerization of methyl acrylate ($[M]_0 = 11.1$ M) at 22 °C, 80% conversion being reached within 2 h.[20] They showed that the choice of ligand for the Cu^{I} catalyst was critical for an efficient polymerization: much slower rates were obtained with a dialkyl-substituted bipyridine ligand than with a multifunctional ligand, hexamethylated tris[2-(dimethylamino)ethyl]-amine. Recently, Wang and co-workers reported the rapid ATRP of a hydrophilic monomer, monoethoxy-capped oligo(ethylene oxide) methacrylate, in aqueous media ($[M]_0 \approx 1.5$ M) at ambient temperature, using $Cu^{I}Cl$/2,2′-bipyridine catalyst.[21] Over 95% conversion was obtained in a short reaction time (<0.5 h).

To prepare well-defined block copolymers (e.g., LC/Iso block copolymers), which is our final goal, the halogenated chain ends must remain intact after the first polymerization in order to initiate the polymerization of another monomer. The mild conditions of the ATRP described in this paper may be very helpful for this chain-end preservation.

Mesomorphic Properties

Side-On Polymethacrylates **P1** and **P2**

The monomers **M1** and **M2** present a nematic (N) phase. **M1** is nematic monotropic: Cr 82.8 I (1 °C · min^{-1}); Iso 79.4 N 60 Cr (−1 °C · min^{-1}) (Cr represents the crystalline phase). **M2** is nematic enantiotropic: Cr 83.2 N 85.5 I (1 °C · min^{-1}); Iso 84.8 N 53 Cr (−1 °C · min^{-1}). The corresponding polymers **P1** and **P2** are all nematic enantiotropic. Schlieren-type textures were observed in their nematic phase. For comparison, we also polymerized **M1** and **M2** by the conventional radical method. The polymers obtained (**P1-rad** and **P2-rad**) have a similar value of $\overline{M}_n$, but larger polydispersity, compared with the polymers synthesized by ATRP (see Table 2). The DSC thermograms of **P1-1**, **P1-2** and **P1-rad** are shown in Figure 7, those of **P2-1**, **P2-2** and **P2-rad** in Figure 8. We can see clearly that N–Iso transitions are narrow and sharp for the polymer samples prepared by ATRP, due to their narrow molecular-weight distribution. However, N–Iso transitions are large and diffuse for the samples prepared by conventional radical polymerization, because of their large molecular-weight distribution. The transition

Table 2. LC polymethacrylates obtained by conventional radical polymerization.

Polymer	Monomer	$\overline{M}_n$ / Dalton	$\overline{M}_w$ / Dalton	DP_n[a)]	$\overline{M}_w/\overline{M}_n$
P1-rad	**M1**	79660	184900	123	2.32
P2-rad	**M2**	100600	168200	167	1.67

[a)] DP is the degree of polymerization.

Table 3. Transition temperatures taken as the peak temperatures in DSC thermograms (°C) and enthalpies (in brackets) (J · g^{-1}) obtained by DSC analysis at 5 °C · min^{-1}.

Sample		Glass (g)	Crystalline (Cr)		Smectic A (SmA)		Nematic (N)		Isotropic (Iso)
P1-2	Heating		•[a]	66.2 (6.69)	–		•	85.1 (0.79)	•
	Cooling	•	–[b]	51	–		•	82.4 (0.87)	•
P1-rad	Heating		•	61.0 (6.82)	–		•	85.8 (~0.17)	•
	Cooling	•	–	49	–		•	80.1 (~0.84)	•
P2-2	Heating		•	80.6 (8.20)	–		•	96.7 (0.93)	•
	Cooling	•	–	61	–		•	94.7 (1.00)	•
P2-rad	Heating		•	73.8 (8.12)	–		•	94.9 (~0.23)	•
	Cooling	•	–	57	–		•	90.8 (~1.05)	•
P3	Heating		•	56.0 (5.44), 69 (0.43)[c]	–		•	108.2 (2.07)	•
	Cooling	•	–	33	–		•	106.5 (2.27)	•
P3-rad[d]	Heating	•	–	95	–		•	105 (2.1)	•
P4	Heating	–	•	117.5 (13.75)	•	130.8 (1.6)[e]	•	133.1 (3.9)[e]	•
	Cooling	–	•	105.7 (10.94)	•	130.1 (1.8)[e]	•	131.8 (3.6)[e]	•
P4-rad[f]	Heating		•	117 (32)	–		•	127–131 (7.4)	•
P5	Heating	–	•	48.2 (10.06)	–		–		•
	Cooling	•	–	35	–		–		•

[a] The • symbol means the phase exists.
[b] The – symbol means the phase does not exist.
[c] A flat peak is visible after the sharp melting peak. There are probably two forms of crystals in the polymer.
[d] Polymer prepared from **M3** by the conventional radical method. Data from previous work.[22, 23]
[e] The SmA–N and N–Iso transitions are very close to each other. The enthalpy of each transition was estimated from the partial area shown by the vertical line indicated in Figure 10.
[f] Polymer prepared from **M4** by the conventional radical method. Data from previous work.[25] In another study, the following data were given: Cr 119 °C (12.6 J · g^{-1}) Sm 136 °C (7.1 J · g^{-1}) Iso.[24]

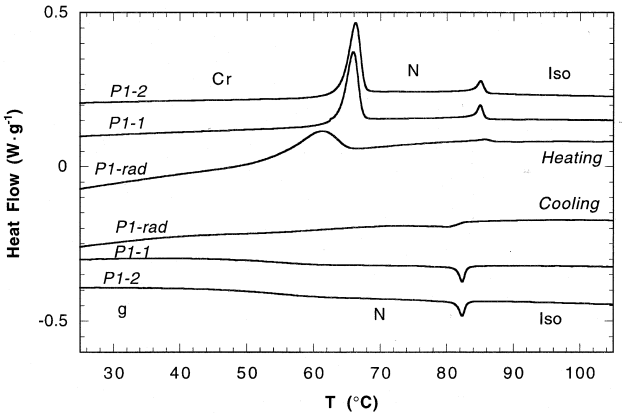


Figure 7. DSC thermograms of polymers **P1-1**, **P1-2** and **P1-rad** on heating and cooling at 5 °C · min^{-1}. **P1-1** and **P1-2** were prepared by ATRP; **P1-rad** was prepared by conventional radical polymerization.

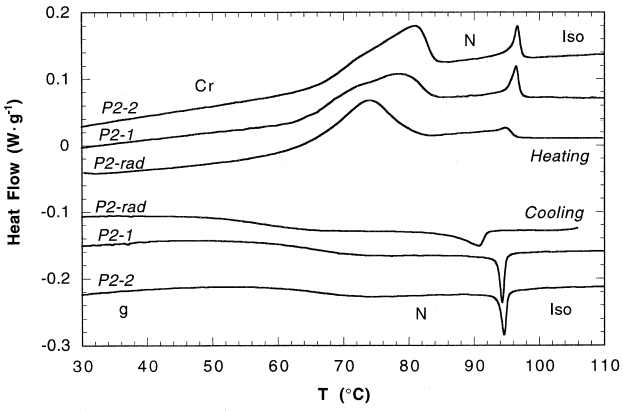


Figure 8. DSC thermograms of polymers **P2-1**, **P2-2** and **P2-rad** on heating and cooling at 5 °C · min^{-1}. **P2-1** and **P1-2** were prepared by ATRP; **P2-rad** was prepared by conventional radical polymerization.

temperatures of **P1-1** and **P1-2** are higher that those of **P1-rad**, and the transition temperatures of **P2-1** and **P2-2** higher than those of **P2-rad**. For the samples obtained by ATRP, the N–Iso transition temperature remains nearly the same in the molecular weight range studied (from $\overline{M}_n$ = 89 000 to 107 000 for **P1** and from $\overline{M}_n$ = 68 000 to 91 000 for **P2**). For **P1-rad** and **P2-rad**, it is difficult to evaluate the transition enthalpies, while we can do it rather precisely for polymers prepared by ATRP. The transition temperatures and enthalpies are listed in Table 3.

Side-End Polymethacrylates **P3**, **P4** and **P5**

In the three side-end monomers, **M3** is nematic monotropic: Cr 49.5 Iso (°C) (1 °C · min^{-1}), Iso 36.3 N 33.1 Cr (–1 °C · min^{-1}); **M4** is smectic (Sm): Cr 63.8 Sm 70.0 Iso (1 °C · min^{-1}), Iso 68.9 Sm 51.9 Cr (–1 °C · min^{-1}); and

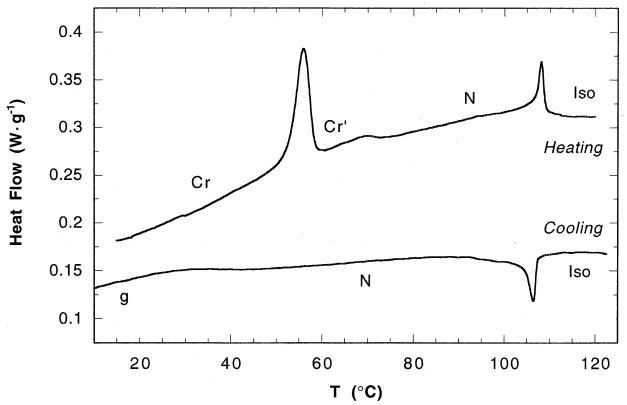


Figure 9. DSC thermograms of polymer **P3** on heating and cooling at 5 °C · min^{-1}.

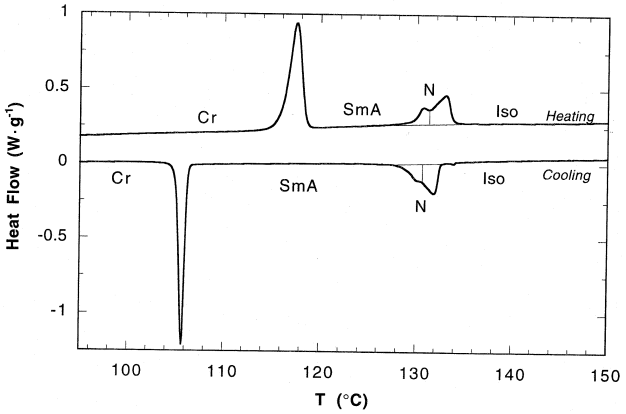


Figure 10. DSC thermograms of polymer **P4** on heating and cooling at 5 °C · min^{-1}.

M5 is not liquid crystalline: Cr 51 Iso (1 °C · min^{-1}). The phases for the corresponding polymers are: **P3** is nematic enantiotropic; **P4** presents nematic and smectic phases; **P5** is not liquid crystalline (see Figure 9, 10 and Table 3). The polymers prepared from **M3** and **M4** by the conventional radical method (**P3-rad**[22, 23] and **P4-rad**[24, 25]) were studied many years ago. In Table 3, we compare our results with those in the literature. The molecular weights and the molecular-weight distributions of **P3-rad**[22] and **P4-rad**[24] were not reported. Thus, it is not appropriate to compare the values of the transition temperatures. Figure 9 shows that the N–Iso transition is narrow and sharp for **P3** obtained by ATRP. For the polymer prepared from **M4**, it was believed that only one LC phase existed. Some authors[25] described this phase as a nematic phase and others as a smectic phase.[24] For our sample **P4**, the DSC thermograms show clearly the existence of two LC phases (Figure 10), even though the second one exists in a narrow range between 130 and 133 °C. Similar DSC thermograms were observed for **P4-rad**, but it was suggested that the N–Iso transition happened in two steps near 130 °C.[25] The polydispersity of **P4** obtained by ATRP is rather narrow ($\overline{M}_w/\overline{M}_n = 1.45$), so we think that

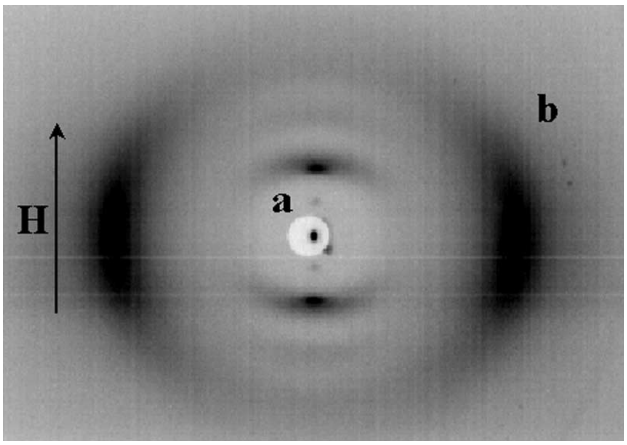


Figure 11. X-ray diffraction pattern of **P4** in the smectic A phase ($T = 120$ °C) (a) small-angle Bragg reflections; (b) wide-angle reflection. **H** is the direction of the applied magnetic field.

the two peaks near 130 °C correspond to two phase transitions and that the two phases would be a smectic phase and a nematic phase, respectively. Optical observation confirms this assignment. Prolonged annealing at a temperature close to, but below, the Sm–N transition led to the formation of a fan-shaped texture. In order to confirm further this assignment and to know what kind of smectic phase it is, we performed X-ray diffraction on an aligned sample of **P4**. Figure 11 shows the X-ray diffraction pattern done at $T = 120$ °C. It corresponds to an aligned smectic A (SmA) structure. Small-angle Bragg reflections (a) are due to smectic layers, and wide-angle reflection (b) are associated with molecular arrangements of mesogenic side groups within the smectic layers. Reflection at wide-angles located near the equator indicate the liquid-like arrangement of the mesogens aligned macroscopically in a direction parallel to the magnetic field. The average distance between side groups is estimated at 4.5 Å. Because of the form factor, the first order of Bragg reflections has almost vanished, and only the second order can clearly be seen. The smectic layer spacing d associated with the Bragg reflections is 27.8 Å. The extended molecular length of the side group is estimated at 21–22 Å. Therefore, a one-layer anti-parallel packing[23] is more probable for the SmA structure. Near to the Bragg reflections, there are diffuse streaks probably linked to the presence of defects in the structure.[26] In spite of its narrow temperature range, the nematic phase was also studied by X-ray scattering, and wide-angle diffuse crescents near the equator were seen. The phase sequence of **P4** is then Cr–SmA–N–Iso.

Conclusion

We demonstrate in this work that ATRP is a good practical method for preparing side chain (side-end and side-on) LC polymers. The obtained polymers have low poly-

dispersities, adjustable molecular weights and are quite suitable for the investigation of structure/property relationships.

Side-on LC polymers prepared by ATRP are of particular interest for us since our goal is the synthesis of well-defined Iso/LC/Iso triblocks copolymers. These triblock copolymers have been proposed recently by de Gennes[27] as suitable model systems in the preparation of new artificial muscles.

In the work reported here, we have succeeded in the synthesis of monodisperse side-on LC polymers by ATRP in mild conditions, using either a monofunctional or a difunctional initiator. The mild conditions (room temperature and rather low concentrations) should be favorable for the preservation of the chain-end functions in the perspective of preparing block copolymers. From the kinetic studies, we have shown that, when using the difunctional initiator, the polymerization proceeds from the two chain-ends with similar efficiencies and displays first-order kinetics.

Efforts are now being made to improve the ATRP of side-on LC monomers (better molecular-weight control and efficient chain-end preservation), and to prepare LC block copolymers. Results will be reported in a forthcoming paper.

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