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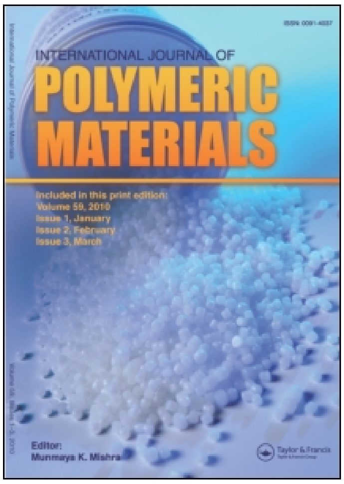

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Synthesis by ATRP and Properties of Liquid Crystalline Three-Armed Star Polymers Containing Azobenzene Chromophores

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Synthesis by ATRP and Properties of Liquid Crystalline Three-Armed Star Polymers Containing Azobenzene Chromophores

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Atom Transfer Radical Polymerization (ATRP) has been applied to synthesize liquid crystalline methacrylic polymers having three-arms star structure, starting from a central core of C_3 symmetry. By just changing the duration of the polymerization process, macromolecules having distinct average chain lengths with low polydispersity values and well defined end-groups have been obtained. All the obtained star-shaped polymers, characterized by differential scanning calorimetry and polarized optical microscopy, exhibit smectic and nematic liquid-crystalline phases on heating, with transition temperatures strongly dependent on the average polymerization degree, and high clearing points. The comparison of these systems with the analogous linear derivatives pointed out higher glass transition temperature values, although they are characterized by lower average polymerization degree. Such behavior can be attributed to the stiffness of the aromatic core, which limits the free movement of chain ends.

Keywords: atom transfer radical polymerization, azobenzene-containing polymers, photochromic polymers, side-chain liquid crystalline polymers, star polymers

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INTRODUCTION

Recently, intensive research activities have been directed toward the development of materials for recording, transfer, and processing of data. In this context photochromic liquid crystalline polymer systems have become of great interest because they combine the physicochemical properties of macromolecular compounds, the mesomorphic properties of liquid crystals, and the photosensitivity of chromophores anchored to the main chain as side-groups [1].

Among these materials, polymers functionalized with azobenzenes seem to be one of the most suitable materials for holographic storage [2–3], photoorienting layers of liquid crystalline displays [4], and artificial muscles [5].

It is well known that several mesophases in side-chain liquid crystalline polymers (SCLCPs) appear only in polymers fractions composed of longer macromolecules [6–7]. However, little attention has been paid in the literature to the influence of macromolecular structure (linear, branched, star, etc.), polymerization degree and polydispersity index ($\overline{M}_w/\overline{M}_n$) on the properties of SCLCPs containing azodyes.

The authors have therefore been interested in synthesizing a series of star-shaped liquid crystalline polymers consisting of three linear chains linked to a central core of aromatic nature. This class of compounds is very attractive because of their physical properties and possible processing advantages derived from their compact structures.

These systems have been obtained by Atom Transfer Radical Polymerization (ATRP), which is one of the most successful methods for the synthesis of macromolecules with controlled molecular weight and molecular weight distribution [8]. This procedure is in fact very versatile, being suitable to polymerize a wide range of monomers, insensitive to many functional groups and tolerant toward impurities present in solvent and reactants, including water. Several methacrylic esters have been successfully polymerized by this method, for example n-butyl methacrylate [9–10], fluorinated methacrylic esters [10–11] and 1-phenoxycarbonyl ethyl methacrylate [12], as well as liquid crystalline (LC) polymers containing azoaromatic moieties in the side-chain [13–15].

Accordingly, the authors have polymerized the monomer 4-ω-methacryloyloxy-hexyloxy-4′-ethoxyazobenzene (**M6A**) by ATRP, using 1,3,5-(2′-bromo-2′-methyl-propionato)benzene (**BMPB**) as the initiator of radical living polymerization and the transition metal salt Cu(I)Br, in combination with 1,1,4,7,10,10-hexamethyltriethylenetetramine

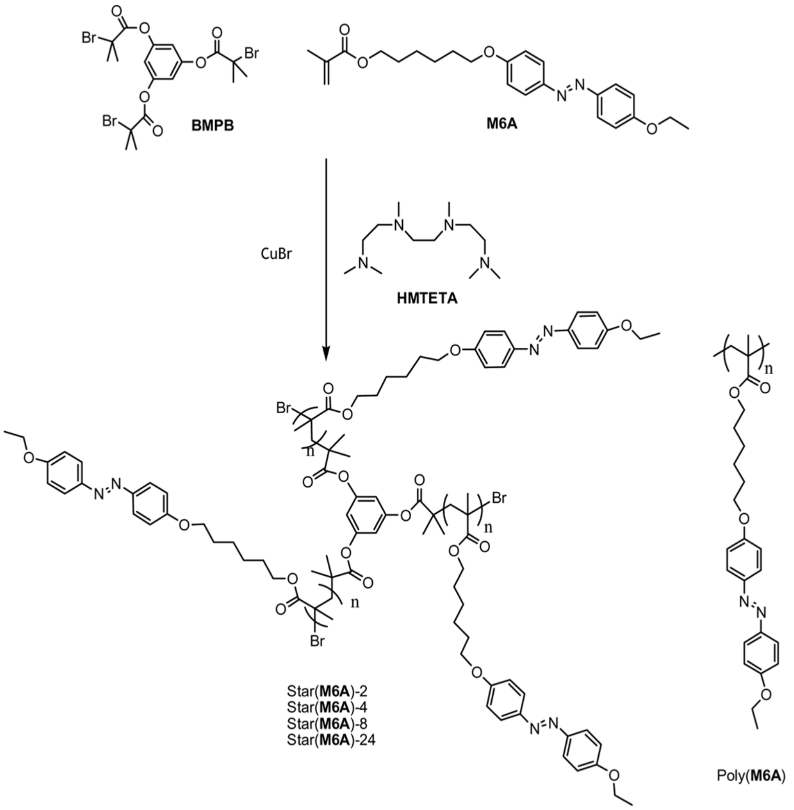

FIGURE 1 Synthesis of star(**M6A**) polymers by ATRP and structure of linear poly(**M6A**).

(**HMTETA**) as ligand. This method has allowed us to obtain LC macromolecules [Star(**M6A**)] having the same C_3 symmetrical aromatic central core (Figure 1) and variable average chain length with low polydispersity just by varying the process duration.

All the derivatives have been characterized by usual spectroscopic techniques and their liquid-crystalline behavior investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). With the aim to investigate the structure–property relationships of these systems, they have been compared with the analogue linear polymer [Poly(**M6A**)] with $\overline{M}_w = 74000$, $\overline{M}_w/\overline{M}_n = 1.9$, previously reported in the literature [16] (Figure 1) and obtained by AIBN free radical polymerization of the corresponding monomer.

EXPERIMENTAL

Physico-Chemical Measurements

^{1}H- and ^{13}C-NMR spectra were obtained at room temperature, from 5–10% $CDCl_3$ solutions, using a Varian NMR Gemini 300 spectrometer. Chemical shifts are given in ppm from tetramethylsilane (TMS) as the internal reference. ^{1}H-NMR spectra were run at 300 MHz by using the following experimental conditions: 24,000 data points, 4.5-kHz spectral width, 2.6-s acquisition time, 128 transients. ^{13}C-NMR spectra were recorded at 75.5 MHz, under full proton decoupling, by using the following experimental conditions: 24,000 data points, 20-kHz spectral width, 0.6-s acquisition time, 64,000 transients.

FT-IR spectra were obtained by a Perkin-Elmer 1750 spectrophotometer, equipped with an Epson Endeavour II data station, on samples prepared as KBr pellets.

UV-Vis absorption spectra of the samples in solution were recorded at 25°C in $CHCl_3$ on a Perkin-Elmer Lambda 19 spectrophotometer.

The spectral region 650–250 nm was investigated by using cells path length of 1 and 0.1 cm. Concentrations of azobenzene chromophore of about $3.0 \times 10^{-4}\,\mathrm{mol \cdot L^{-1}}$ were used.

Number average molecular weights of the polymers ($\overline{M}_n$) and their polydispersity indexes ($\overline{M}_w/\overline{M}_n$) were determined in THF solution by SEC using HPLC Lab Flow 2000 apparatus, equipped with an injector Rheodyne 7725i, a Phenomenex Phenogel 5-micron MXL column and a UV-VIS detector Linear Instrument model UVIS-200, working at 254 nm. Calibration curve was obtained by using monodisperse polystyrene standards in the range 800–35,000.

The glass transition temperature values were determined by differential scanning calorimetry (DSC) on a TA Instrument DSC 2920 Modulated apparatus at a heating/cooling rate of 10°K/min under nitrogen atmosphere on samples weighing 5–9 mgr.

Optical microscopy observations were performed on polymer films obtained by casting on glass slides with a Zeiss Axioscope2 polarizing microscope through crossed polarizers fitted with a Linkam THMS 600 hot stage.

Materials

The monomer 4-ω-methacryloyloxy-hexyloxy-4′-ethoxyazobenzene (**M6A**) was synthesized as previously reported [16]. THF was purified and dried according to the reported procedures [17] and stored under nitrogen. The trifunctional initiator 1,3,5-(2′-bromo-2′-methylpropionato)benzene (**BMPB**) was prepared as previously described [18–19];

1,1,4,7,10,10-hexamethyltriethylenetetramine (**HMTETA**), copper bromide, and all the other reagents and solvents (Aldrich) were used as received.

Synthesis of C_3-Symmetrical Polymers by ATRP

All homopolymerizations of **M6A** were carried out in glass vials using **BMPB** as the initiator, **HMTETA** as the ligand, Cu(I)Br as catalyst in dry THF [**M6A**/THF 1/20 g/ml]. Every mixture [**M6A**/**BMPB**/**HMTETA**/CuBr = 150:1:3:3 by mol] was introduced into several vials under nitrogen atmosphere, submitted to several freeze-thaw cycles, and heated at 60°C. To terminate the polymerization reaction, the vials were frozen in liquid nitrogen after known reaction times, ranging from 2 to 24 h. The obtained product was purified by precipitation in a large excess of cold methanol and the coagulated polymer [Star(**M6A**)-2 through Star(**M6A**)-24] filtered off, redissolved in $CHCl_3$, precipitated again with cold methanol and finally dried at 70°C under vacuum for one day to constant weight. Relevant data for the synthesized derivatives are reported in Table 1. All the products were characterized by FT-IR, ^1H- and ^{13}C-NMR. As an example, the spectroscopic data for Star(**M6A**)-24, obtained after 24 h of reaction, are here reported.

^1H-NMR ($CDCl_3$): 7.80 (m, 4H, 2- and 2′-H), 6.90 (m, 3H, arom core and 4H, 3- and 3′-H), 4.10–3.80 (m, 6H, $CH_2{-}O$), 2.20 ($CH_2{-}C{-}Br$), 1.95 (m, 3H, $CH_3{-}C{-}Br$), 1.80–1.40 (m, 8H, aliph spacer CH_2 and 3H, main chain CH_3), 1.40–0.80 (m, 18H, $C(CH_3)_2{-}COO$ and 3H, $C\mathit{H}_3{-}CH_2$) ppm.

^{13}C-NMR ($CDCl_3$): 178.6 and 178.1 (CO repeating unit), 167.8 (CO core), 161.7 and 161.6 (arom 4-C and 4′-C), 153.1 (C−O arom core), 147.6 (arom 1-C and 1′-C), 125.0 (arom 2-C and 2′-C), 115.3 (arom 3-C and 3′-C), 113.1 (arom C−H core), 68.7 ($CH_2{-}\mathit{C}H_2{-}O{-}$),

TABLE 1 Characterization Data of Star Polymeric Derivatives

Samples	Reaction time (h)	Yield[a] (%)	$\overline{M}^{b}_{n,th}$ (g/mol)	$\overline{M}^{c}_{n,SEC}$ (g/mol)	$\overline{M}_w/\overline{M}^c_n$
Star(**M6A**)-2	2	8	5600	5900	1.21
Star(**M6A**)-4	4	13	8600	7800	1.12
Star(**M6A**)-8	8	30	19000	17400	1.08
Star(**M6A**)-24	24	70	43700	24900	1.14

[a] Calculated as (g of polymer/g of monomer) · 100.

[b] $\overline{M}_{n,th}$ = Conversion · $(M_{\mathbf{M6A}}/M_{\mathbf{BMPB}}) \cdot MW_{\mathbf{M6A}} + MW_{\mathbf{BMPB}}$.

[c] Determined by SEC in THF at 25°C.

65.7 (CH_3-CH_2-O-), 64.4 ($COO-CH_2-$), 58.0 ($C(CH_3)-Br$), 55.0 (main chain $C-CH_2$), 45.8 and 45.5 (main chain CH_2-C), 42.2 ($C(CH_3)_2-CH_2$), 38.9 ($CH_2-C(CH_3)-Br$), 27.5 ($C(CH_3)-Br$), 29.8, 28.8, 26.6, 26.4 (aliph spacer CH_2), 23.2 ($C(CH_3)_2-CH_2$), 19.3 and 17.5 (main chain CH_3), 15.4 (CH_3-CH_2) ppm.

FT-IR (KBr): 3068 (ν_{CH} arom), 2977 and 2866 (ν_{CH} aliph), 1724 (ν_{CO} ester of the repeating unit and arom core), 1598 ($\nu_{C=C}$ arom), 1392 (ν_{CH} CH_3), 1145, 1113 (ν_{CO} ether), 839 (δ_{CH} 1,4-disubst. arom ring) cm^{-1}.

RESULTS AND DISCUSSION

Synthesis and Characterization

Well-defined LC star-shaped homopolymers were obtained by polymerization of **M6A** in the presence of **BMPB** and Cu(I)Br with **HMTETA** as ligand.

The occurrence of polymerization involving the methacrylic double bond was confirmed by FT-IR, showing the disappearance of the band at 1640 cm^{-1} related to the stretching vibration of the double bond in the monomer, and by ^{1}H-NMR spectra, in which the resonances at 5.60 and 6.10 ppm related to the vinylidenic protons of monomer **M6A** are absent.

In the ^{1}H-NMR spectra the signals related to the aromatic and aliphatic protons of the central core are overlapped on those of the repeating units. The sample obtained at lower reaction times [Star(**M6A**)-2] displays the resonances of the methylene and methyl groups bonded to the quaternary carbon atom bearing the terminal Br atom at 1.9 and 2.3 ppm, respectively. Their intensity decreases by increasing the reaction time and becomes progressively obscured by the more intense resonances related to the aliphatic protons of the main chain, thus preventing assessment of the number average molecular weight of each sample directly by integration of the NMR signals. As an example, Figure 2 reports the ^{1}H-NMR spectrum of Star(**M6A**)-24.

The living character of the polymerization is confirmed by ^{13}C-NMR spectra, which display signals related to the quaternary carbon atom bonded to Br at 58.0 ppm and to the methyl and methylene carbon atoms of the growing chain end-group at 27.5 and 38.9 ppm, respectively.

Figure 3 shows a linear relationship between $\ln([M]_0/[M]_t)$ (where $[M]_0$ and $[M]_t$ are the initial and at t time monomer concentrations, respectively) and the reaction time, thus indicating a first-order kinetics of the polymerization rate with respect to the monomer concentration and a relatively constant concentration of the growing species throughout the process.

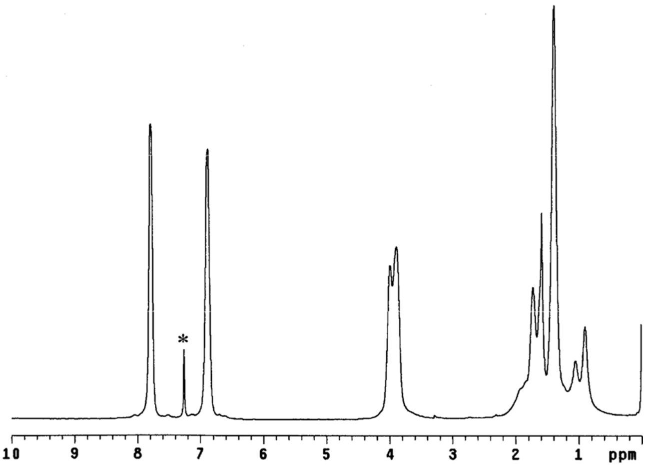

FIGURE 2 ^{1}H-NMR spectrum of Star(**M6A**)-24 in $CDCl_3$. Starred signal refers to solvent resonances.

The data reported in Table 1 show that yields and number average molecular weight values of the obtained polymers are strongly dependent on the reaction time: by varying this last parameter only, it is

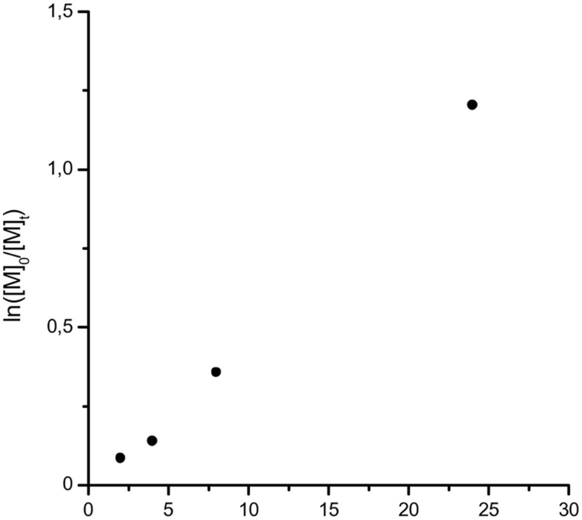

FIGURE 3 Time dependence of $\ln([M]_0/[M]_t)$ in the ATRP of **M6A** in THF.

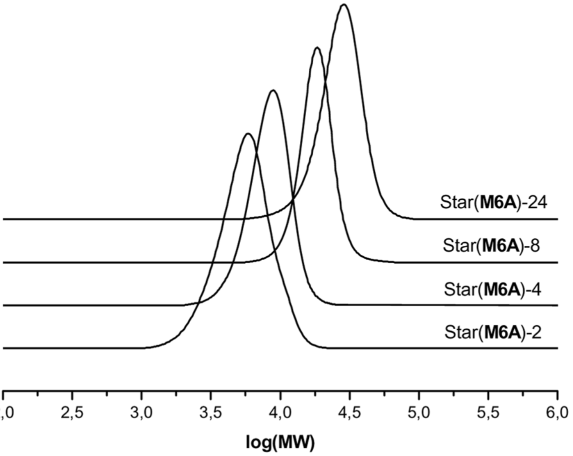

FIGURE 4 Normalized molecular weight distributions of star polymers as determined by SEC in THF at 25°C.

actually possible to modulate the macromolecular chain length, as shown by SEC chromatograms reported in Figure 4.

The plot of the number average molecular weight of the resulting star-shaped polymers as determined by SEC ($\overline{M}_{n,SEC}$) against monomer conversion (calculated by unreacted monomer collection from polymerization mixture) is shown in Figure 5. The theoretical values of $\overline{M}_n(\overline{M}_{n,th})$, that are valid only in the absence of chain termination and transfer reactions, may be calculated by the following equation [20]:

$$\overline{M}_{n,th} = \text{Conversion} \cdot (M_{\mathbf{M6A}}/M_{\mathbf{BMPB}}) \cdot MW_{\mathbf{M6A}} + MW_{\mathbf{BMPB}} \qquad (1)$$

where $M_{\mathbf{M6A}}$ and $M_{\mathbf{BMPB}}$ are the initial amounts in moles of monomer and trifunctional initiator, respectively, and $MW_{\mathbf{M6A}}$ and $MW_{\mathbf{BMPB}}$ their respective molecular weights. As reported in Figure 5, calculated and SEC values are coincident only at low values of monomer conversion but, as the conversion increases, they diverge to an increasing extent. Such a behavior, previously reported for star-shaped chiral photochromic polymethacrylates [21], cannot be ascribed to termination reactions taking place under the real polymerization conditions, as proved by the low and almost constant values of $\overline{M}_w/\overline{M}_n$ (in the range 1.08–1.21), reported in Table 1, but to the particular molecular structure of multiarms polymers. It is well known, in fact, that star polymers have a smaller hydrodynamic volume with respect to that of linear polystyrenes having the same molecular weight. As a consequence SEC analysis gives underestimated molecular weight values

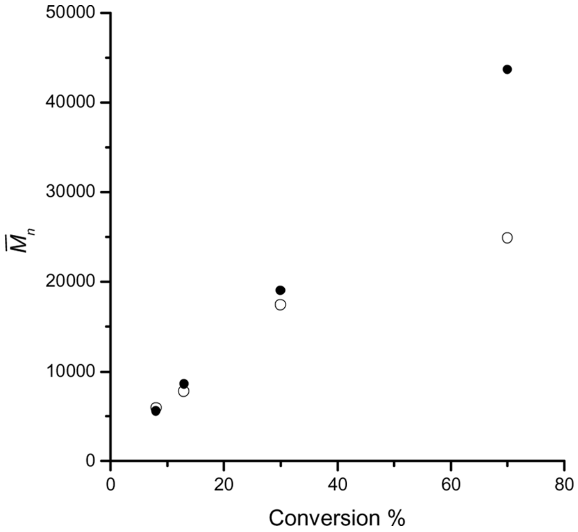

FIGURE 5 Evolution of the number average molecular weight determined by SEC in THF at 25°C (○) and calculated values (●) versus conversion in the ATRP of **M6A**.

for star-shaped polymers when measured with reference to the usually adopted linear polystyrene standards [22–23].

Anyway, the approximately linear correlation between $\overline{M}_{n,SEC}$ and monomer conversion is indicative of the living character of the ATRP process and SEC analysis proves to be useful to confirm that a steady increment of the average molecular weight with conversion has taken place.

In conclusion, all the instrumental characterization techniques confirm that three-arms star polymers with C_3 symmetry and varying molecular size have been successfully obtained. Each chain contains a bromine atom as end group that could be replaced through a variety of reactions leading either to end-functionalized polymers or used as the initiating site for the polymerization of a different monomer to obtain novel star-shaped block copolymers.

The UV-Vis absorption spectra in $CHCl_3$ solution of all the investigated star polymers, as well as the monomer **M6A**, exhibit, in the 250–650 nm spectral region, two bands related to the n–π^* and π–π^* electronic transitions of the azobenzene chromophore in *trans*-configuration with maxima centered at about 360 nm ($\varepsilon \cong 28000$ $L \cdot mol^{-1} \cdot cm^{-1}$) and 440 nm ($\varepsilon \cong 1500\,L \cdot mol^{-1} \cdot cm^{-1}$), respectively [24] and within the limits of experimental error they appear qualitatively and quantitatively independent of branching and polymerization degree.

Thermal Properties and Polarized Optical Microscopy Characterization

With the aim to study their LC properties, all the polymeric derivatives have been characterized by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Phase-transition temperatures determined by DSC are summarized in Table 2: all the macromolecules display on heating a glass-transition temperature (Tg), a smectic liquid-crystal-phase melting endotherm with a consequent nematic liquid-crystal-phase melting endotherm and finally an isotropization temperature (Ti). In all cases, on cooling, the latter transitions show a modest degree of supercooling (4–7°C), whereas this effect is much pronounced for smectic-nematic transition and a stable frozen nematic mesophase is obtained and maintained at room temperature. Figure 6 reports, as an example, the first cooling and the second cycle heating curves for the sample Star(**M6A**)-8.

The smectic (S_{A1}) and nematic (N) liquid-crystalline phases have been identified by the observation of their typical optical texture by POM and confirmed by comparison of their DSC traces with that one of poly(**M6A**), extensively studied by DSC, POM, and X-ray diffraction [16]. Indeed, the LC texture and the thermal properties of Star(**M6A**) homopolymers are in agreement with those of poly(**M6A**) with the expected differences in the transition temperatures values (Table 2). The transition temperatures appear strongly dependent on the polymerization degree, the glass (Tg), the smectic-nematic (T_{SM}) and the nematic–isotropic transition temperatures (Ti) of the series diminishing with the decrease of chain length (Figure 7).

TABLE 2 Thermal Properties of the Polymers Containing **M6A**[a]

Sample	Liquid-crystal transition temperatures [heating (10°C/min)]						
Poly(**M6A**)[b]	G	70	S_{A1}	97	N	152	I
Star(**M6A**)-2	G	57	S_{A1}	78	N	124	I
Star(**M6A**)-4	G	57	S_{A1}	80	N	127	I
Star(**M6A**)-8	G	71	S_{A1}	87	N	142	I
Star(**M6A**)-24	G	85	S_{A1}	94	N	150	I

[a] Obtained from the second DSC thermal cycle.

[b] Reference [16].

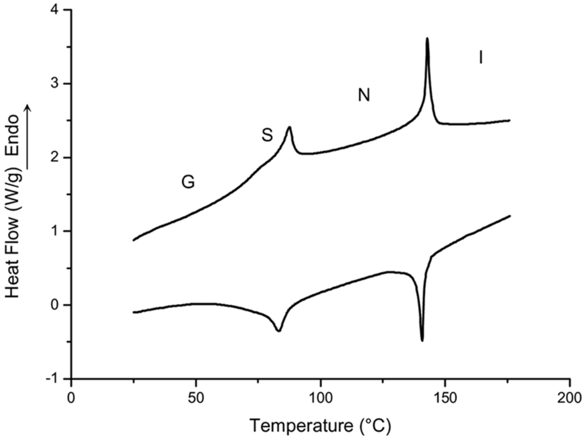

FIGURE 6 DSC cooling (first scan) and heating curves (second scan) for Star(**M6A**)-8.

In particular, the Ti and T_{SM} values of Star(**M6A**)-2 to Star(**M6A**)-24 increase from 124° to 150°C and from 78° to 94°C (Table 1) approaching the maximum values of 152° and 97°C, respectively, found for poly(**M6A**) with $\overline{M}_w = 74{,}000$, obtained by AIBN-initiated free radical polymerization [16]. Interestingly, Star(**M6A**)-8 and Star(**M6A**)-24 show higher Tg than the corresponding linear derivative, this finding being attributable to the stiffness of aromatic core,

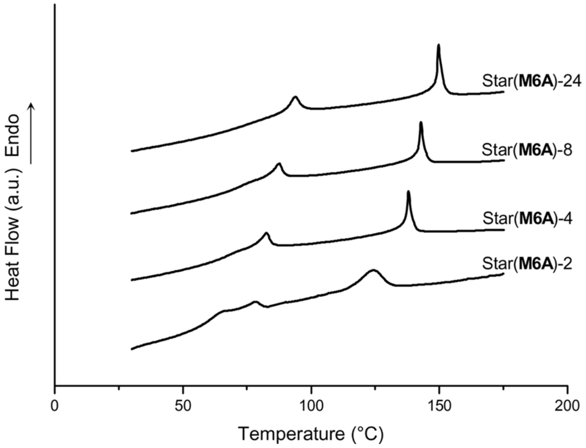

FIGURE 7 DSC heating curves (second scan) for star-shaped polymers.

which limits the free movements of one chain end, thus favoring the macromolecules to increase the extent of interchromophore interactions with respect to the related linear sample. As a consequence, the polymeric samples characterized by lower average molecular weight show wider smectic phase (S_{A1}) ranges and, similarly to the other polymeric samples, a liquid crystalline nematic phase stable for approximately 50 degrees.

CONCLUSIONS

Atom Transfer Radical Polymerization has been successfully used to prepare a series of three-arms star-shaped liquid crystalline polymers with different average molecular weights and low polydispersity.

The living character of the ATRP process is confirmed by the first-order kinetics, a linear molecular weight-conversion profile and narrow molecular weight distribution. Therefore the obtained photochromic LC star polymers could be employed to prepare novel block copolymers with interesting properties and potential applications in advanced technologies. The liquid-crystalline behavior of star-shaped polymers has been confirmed by DSC measurements and POM characterization, which have pointed out the presence of smectic and nematic phases. The transition temperatures are in agreement with those of the analogous linear derivatives extensively studied by DSC, POM, and X-ray diffraction and are strongly dependent on the polymerization degree. It is to be noted that star-shaped derivatives show higher glass transition temperature values than the corresponding linear polymers, although they are characterized by lower average polymerization degree. This finding can be attributed to the stiffness of aromatic core, which prevents the possibility of free movements by part of the macromolecular chain ends.

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