Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 45 (2004) 3637–3642

polymer

www.elsevier.com/locate/polymer

Synthesis and characterization of four-armed star mesogen-jacketed liquid crystal polymer

Xingzhu Wang, Hailiang Zhang*, Guanqun Zhong, Xiayu Wang

Institute of Polymer Science, Xiangtan University, Xiangtan 411105, Hunan Province, People's Republic of China

Received 10 September 2003; received in revised form 23 February 2004; accepted 25 February 2004

Abstract

The synthesis of four-armed star mesogen-jacketed liquid crystal polymer was achieved by atom transfer radical polymerization in chlorobenzene solution using pentaerythritol terakis(2-bromoisobutyrate) (PT-Br) as an initiator and CuBr/sparteine complex as a catalyst. The results show that the number average molecular weigh is creased linearly vs. monomer conversion, and that the polydispersities were quite narrow (<1.19), which is the character of controlled polymerization. The structure was experimentally confirmed by ^{1}H NMR. The liquid-crystalline behavior of the four-armed star polymer was studied using DSC and POM. Only the polymer with a $M_{n,GPC}$ beyond 3.68×10^4 g/mol formed a liquid crystalline phase which was quite stable with a high clearing point.

Keywords: Mesogen-jacketed liquid crystal polymer; Atom transfer radical polymerization; Star-shaped polymer

1. Introduction

Star polymers have become of interest in recent years [1] because of their unique properties and important applications [2–6]. Although preparation of star polymers has been documented as early as 1948 by Schaetgen and Flory [7], the preparation of well-defined multiarm polymers remained a challenge until the advent of living polymerization techniques. This is because precise control of the polymerization is crucial to the synthesis of such multiarm polymers. With the discovery of living anionic polymerization, Morton and co-workers in 1956 [8] were able to take advantage of the method to synthesize well-defined four-armed polystyrenes for the first time by neutralizing living poly(styryllithium) with tetrachlorosilane. Although the product was a mixture of four-and three-arm stars, this work eventually led to many researchers taking on the challenge. As a consequence, the use of anionic living polymerization for the preparation of star polymers dominates the current literatures.

Regardless of the method of polymerization (ionic, metathesis, group transfer, or radical), preparations of star polymers have been practiced using two different methodologies, the so-called, arm-first [9,10] and core-first [11–13] methods. In the arm-first approach, the linear arms of the star polymer are synthesized first followed by binding of the arms to form the core. The binding of the arms is achieved by using either a difunctional monomer or a multifunctional terminating agent. The core-first method involves the synthesis of a multifunctional initiator (the core) followed by the extension of arms by monomer addition.

The applicability of living/controlled radical polymerization techniques in the synthesis of star polymers is well documented in the literature [14] of those that use the arm-first approach, atom transfer radical polymerization (ATRP) [15], nitroxide-mediated polymerization (NMP) [16] and iniferter techniques [17] with divinylbenzene as a binder of the core are prominent. Methods to prepare multiarm polymers using reversible addition-fragmentation chain transfer (RAFT) polymerization [18] were reported recently. Between the two methods, the core-first approach with radical initiator has received greater attention, since it is easy to control the structure of star polymer. For example, Matyjaszewski et al. [19] reported the synthesis of polystyrene and poly(butyl acrycate) star polymers using hexakis (4-hydroxymethylphenoxy) cyclotriphosphazene as multifunctional initiator by ATRP. Sawamoto and co-workers [20] reported the synthesis of poly(methyl

---

* Corresponding author. Tel.: +86-732-8293717; fax: +86-732-8293264.

E-mail address: hailiangzhang@water.pku.edu.cn (H. Zhang).

0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.02.054

methacrylate) star polymer with four, six and eight arms by using calixavene-core multifunctional initiators. Pugh et al. have synthesized three-arm star side chain liquid crystal polymer (LCP) by ATRP [21] and Gnanou [22] Hawker et al. [23] have also contributed much to this area. Use of nitroxide-mediated living polymerization in the construction of star polymers has been reviewed by Hawker et al. [24]. Recently, we demonstrated that 2,5-bis[(4-methoxyphenyl)oxycarbonyl] styrene(MPCS) monomers could be used to confer living character to radical polymerization [25,26], however, there have been no syntheses of star polymers comprising MPCS units, which should exhibit unique properties.

PMPCS represents one of the novel type side-chain liquid-crystal polymers (MJLCPs) [27]. In contrast to conventional side-chain liquid-crystal polymers as regards molecular architecture, the mesogenic units of MJLCPs are linked to the main chain through no or only short spacers by lateral attachment. For PMPCS, only a covalent bond is used to connect to main chain and mesogenic unit. The high population of rigid, bulky side-groups would form a jacket along the polymer chain and thereby force the main chain to take extended or rod-like conformation. Early studies on lytropic behavior, banded texture and solution properties have proved the rod-like nature of MJLCPs [28, 29]. In this article, we report the synthesis and structure of four-armed star mesogen-jacketed liquid crystal polymer obtained by atom transfer radical polymerization in chlorobenzene solution using pentaerythritol terakis (2-bromoisobutyrate)(PT-Br) as an initiator and CuBr/sparteine complex as a catalyst. The resulting polymers have a predictable molecular weight and a narrow molecular weight distribution. The reaction route is shown in Scheme 1.

2. Experimental

2.1. Materials

Chlorobenzene (Acros.99%) was purified by washing with concentrated sulfuric acid to remove residual thiophenes, followed by washing twice with water, once with 5% sodium carbonate solution, and again with water before being dried with anhydrous calcium chloride and distilled. CuBr was prepared from $CuBr_2$ and purified by stirring in acetic acid, washing with methanol and then drying in vacuum. Sparteine (Sp. from Aldrich) was distilled under reduced pressure over calcium hydride and stored and nitrogen atmosphere at 4 °C in the dark. Tetrahydrofuran (AR; Beijing chemical Co.) was distilled over CaH_2. Other solvents and reagents were used without further purification, except as noted.

2.2. Synthesis MPCS monomer

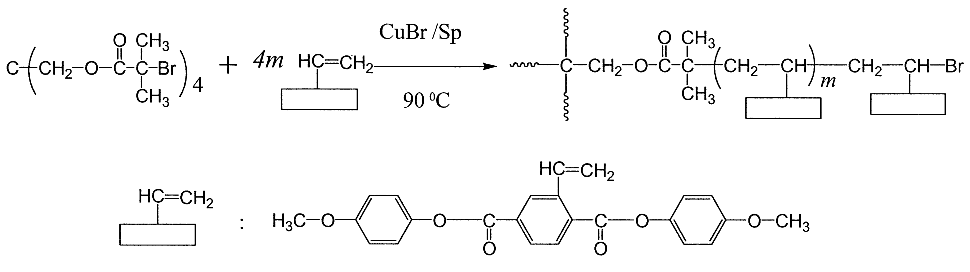
The monomer 2,5-bis[(4-methoxyphenyl) oxycarbonyl]-styrene] (MPCS), was synthesized by the reaction of 2-vinylterephathalic acid according to the method described by Zhang et al. [30], ^1H NMR ($CDCl_3$): $\delta = 3.83$, 6H for OCH_3, 5.1–5.90, 2H for $=CH_2$, 6.60–6.95, 1H for $-CH=$ and 7.00–8.30, 11H for the phenylene rings. As reported earlier [31], MPCS exhibits a smectic phase between its melting temperature 109 °C and LC 144 °C.

2.3. Synthesis of pentaerythritol terakis(2-bromoisobutyrate) (PT-Br)

A 3.7 g (27 mmol) sample of pentaerythritol was placed into a 250 ml round-bottom flask with 100 ml of THF and 12 g (0.12 mol) triethylamine. A solution 26 g (0.12 mol) of 2-bromopropionyl bromide and 20 ml THF was added to a 50 ml pressure equalizing addition funnel fitted to the flask under N_2, the reactor was cooled to 0 °C in a ice/water bath, and the acid halide solution was added dropwise. The reaction was stirred overnight and allowed warm to room of its own accord. The product, a white solid was recrystallized directly from the dithylether. Yield = 8.0 g (42%). Mp = 133–134 °C. ^1H NMR ($CDCl_3$) δ: 4.31 (s, 8H, $C-CH_2-O$), 1.93 (s, 24H, C $(Br)-CH_3$) ppm.

2.4. Polymerization

A dry glass tube was charged with CuBr, MPCS, Sp, PT-Br, and chlorobenzene solution. The mixture was degassed by three freeze-pump-thaw cycles and sealed under vacuum; the tube was placed in an oil bath at the desired temperature maintained by a thermostal. After an expected time, the tube was placed in an ice bath to stop the reaction. The reaction mixture was diluted with THF and added



Scheme 1. Synthetic route of four-armed star mesogen-jacketed liquid crystal polymer.

dropwise into methanol, after filtration and washing two times methanol, followed by drying at 50 °C under vacuum for 24 h, star-shaped PMPCS was obtained. The conversion of the monomer was determined gravimetrically.

2.5. Measurements

The M_n and molecular weight distribution (M_w/M_n) were measured on a WATER 2414 gel permeation chromatography (GPC) instrument with a set of HT3, HT4 and HT5, μ-styrayel columns with THF as an eluent (1.0 ml/min) at 35 °C. Calibration was made with standard polystyrene (PSt). The ^{1}H NMR spectrum was taken at 25 °C on a INOVA-300 NMR spectrometer with chloroform-*d* as a solvent and with tetramethylsilane (TMS) as an internal reference. Thermograms were obtained using a Perkin–Elmer DSC-7 instrument. Polarized optical microscope observation was performed on a Leitz Laborlux 12POL microscope with a Leitz 350 hot stage.

3. Results and discussion

The ATRP of MPCS initiated by PT-Br with CuBr, complexed by Sp, was carried out in chlorobenzene solution at 90 °C. The MPCS, PT-Br, CuBr, Sp molar ratio was 400:1:4:8. Under these conditions, all the reagents, including the MPCS, PT-Br, CuBr, Sp and polymer, were soluble in chlorobenzene, and the reaction medium remained homogeneous throughout the polymerization.

Fig. 1 shows the relationship between ln($[M]_0/[M]$) and the reaction time. The first-order kinetic plots indicate that the living radical concentration was constant during the polymerization. An induction time was observed for the polymerization of MPCS in solution. The reason is not clear at the present time but it is speculated that the residual oxygen might be the cause of induction time [32]. However, the experiment was repeated the same. An alternative explanation might be related to the formation of the actual initiating centre as a result of the interaction between the catalyst complex and initiator [33]. In the free state, it has the transoid structure, but when complexed with a metal ion, it acquires the cisoid shape. The formation of the actual initiation centre might be associated with the conformation change.

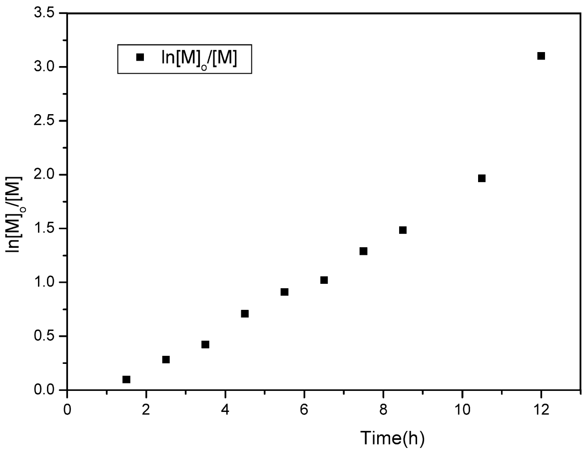


Fig. 1. Time dependence of ln$[M]_0/[M]$ at 90 °C temperature where $[M]_0$ and [M] are the MPCS concentration at 0 and *t*, respectively. Conditions: MPCS/Ph-Cl = 20:80, MPCS/PT-Br/CuBr/Sp = 400:1:4:8.

The plots of M_n and M_w/M_n of resulting star-shape PMPCS against conversion are shown in Fig. 2. With an increase in the monomer conversion, the molecular weight increased, and the polydispersity decreased slightly at first and then remained almost unchanged. The values of M_w/M_n were less than 1.19 implying a well-controlled polymerization process. Fig. 3 shows the GPC curves of the obtained star-shaped polymers, all are narrow and symmetrical.

The results are summarized in Table 1.

As can be seen in Table 1, the molecular weights measured by GPC $M_{n,GPC}$ were much lower than the calculated values, $M_{n,th}$, according to Eq. (1).

$$M_{n,th} = \text{Conversion} \times (M_{MPCS}/M_I) \times 404 + 732 \qquad (1)$$

Where M_{MPCS} and M_I are respectively the initial moles of MPCS and the tertrafunctional initiator (PT-Br); 404 and 732 are the molecular weight of MPCS and PT-Br respectively.

The chemical structure of the obtained star-shaped PMPCS was characterized by 300 MHz ^{1}H NMR spectroscopy. Fig. 4 showed the representative ^{1}H NMR spectrum of the well-defined star-shaped PMPCS with a $M_{n,GPC}$ value of 0.84×10^4 g/mol and M_w/M_n value of 1.19. The peak at $\delta = 1.25$ (a) corresponding to methyl protons. The peak at $\delta = 1.2$–2.60 (b), 6.35–7.20 (d) and $\delta = 7.20$–8.20 (c) representing the methylene protons(peak I_b), methine proton(peak I_b) and aromatic protons(peak I_c, I_d) in PMPCS unit, respectively. The signals at $\delta = 3.30$–4.0 (e) corresponding to the side chain $-OCH_3$ of PMPCS arms (peak I_e). The peak at around $\delta = 4.35$–4.65 ppm (f) corresponds to the methine proton in the monomer unit

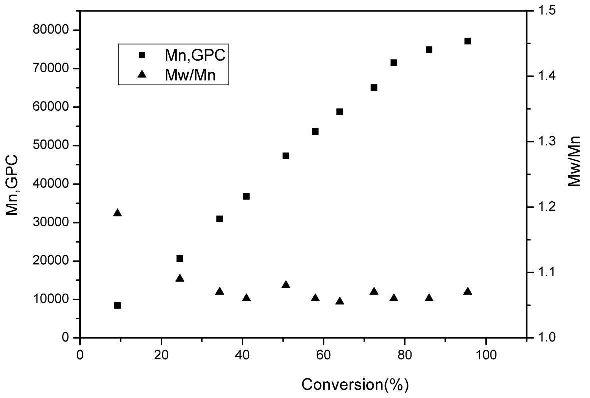


Fig. 2. Dependence of four-armed star mesogen-jacketed liquid crystal polymer the average number molecular weight and polydispersity on the monomer on conversion at 90 °C. Conditions: MPCS/Ph-Cl = 20:80, MPCS/PT-Br/CuBr/Sp = 400:1:4:8.

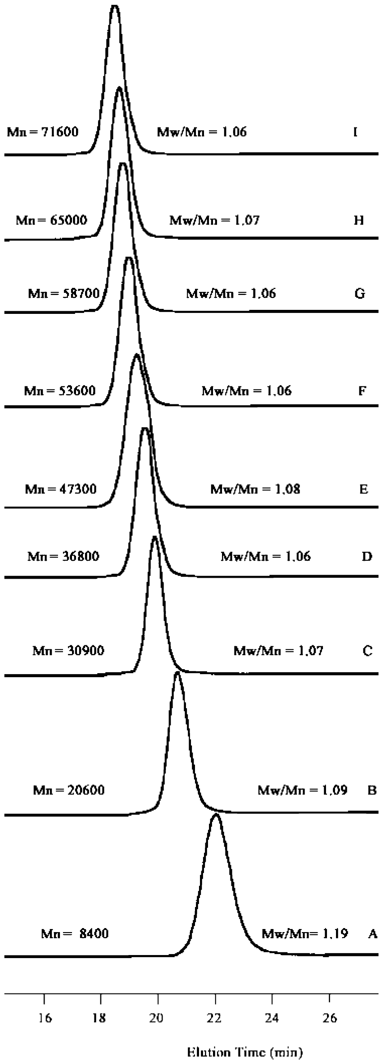


Fig. 3. GPC trace of four-armed star mesogen-jacketed liquid crystal polymers of different $M_{n,GPC}$.

Table 1
GPC NMR DSC date and liquid crystallinity of four-armed star mesogen-jacketed liquid crystal polymers

Polymer	$M_{n,th}$[a] ($\times 10^{-4}$)	$M_{n,NMR}$[b] ($\times 10^{-4}$)	$M_{n,GPC}$[c] ($\times 10^{-4}$)	M_w/M_n	T_g (°C)[d]	T_g (°C)[e]	LC[f]
A	1.57	1.46	0.84	1.19	108.6	106.0	No
B	4.05	3.64	2.06	1.09	110.0	107.0	No
C	5.63	5.12	3.09	1.07	119.6	115.5	No
D	6.70	6.15	3.68	1.06	125.4	119.6	Yes
E	8.44	/	4.73	1.08	129.0	120.5	Yes
F	9.71	/	5.36	1.06	130.8	120.9	Yes
G	10.42	/	5.87	1.06	130.2	123.0	Yes
H	11.78	/	6.50	1.07	130.3	119.4	Yes
I	12.56	/	7.16	1.06	134.5	121.2	Yes
J	13.90	/	7.49	1.06	135.6	122.7	Yes
K	15.44	/	7.71	1.06	136.0	123.1	Yes

[a] $M_{n,th}$ was calculated according to Eq. (1).
[b] $M_{n,NMR}$ was calculated based on proton NMR date.
[c] Measured on water-2414 GPC instrument.
[d] T_g measured at the first heating scan.
[e] T_g measured at the second heating scan.
[f] Phase behavior as observed by polarized optical microscopy.

adjacent to bromine (peak I_f) and the signals at around peak at $\delta = 4.04$ (g) corresponding to methylene protons next ester. It is a proof of the well-defined tetra-armed star-shaped PMPCS with terminal bromine was provided. Based on the integral values of the peaks at $\delta = 3.30$–$4.0(I_e)$ and at $\delta = 4.35$–4.65 ppm (I_f), the $M_{n(NMR)}$ was can be calculated according to Eq. (2), where 4 defines the branch values of the star PMPCS and the values 404, 732 are the molar masses of MPCS,PT-Br, respectively:

$$M_{n(NMR)} = 4(I_e/6I_f) \times 404 + 732 \qquad (2)$$

The results listed in Table 1 show that the $M_{n,GPC}$ values of the star polymers determined by ^{1}H NMR were much larger than the counterparts based on GPC. This may be due to the difference in solvent property between star polymer and standard polystyrene, another reason because star polymers have same molecular weight when the length of arm was

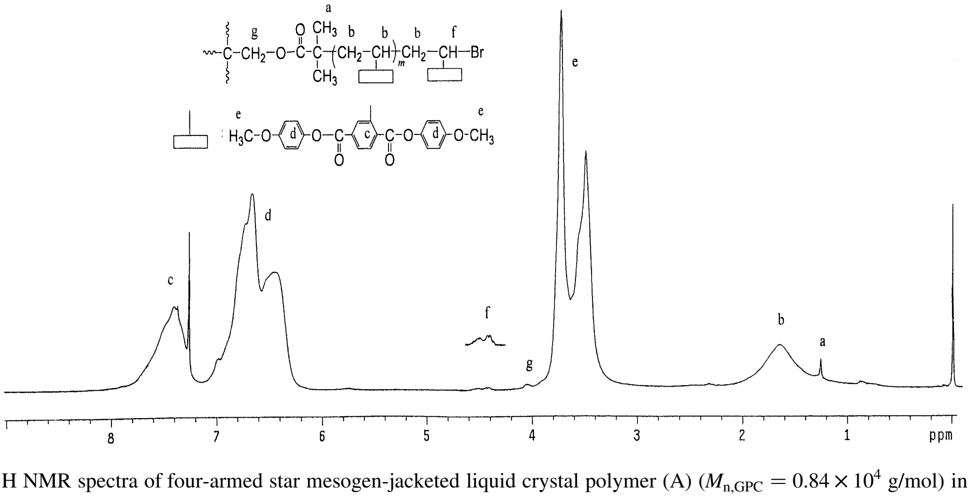


Fig. 4. ^{1}H NMR spectra of four-armed star mesogen-jacketed liquid crystal polymer (A) ($M_{n,GPC} = 0.84 \times 10^4$ g/mol) in $CDCl_3$.

made large, the arm number decreased, and, in turn, the $M_{n,GPC}$ of star decreased. This indicates that a longer arm cause a larger steric hindrance of the four-armed star polymer formation. Then another proof of the well-defined four-armed star-shaped PMPCS was provided.

Thermal analysis was performed with a Perkin–Elmer DSC-7 instrument under nitrogen atmosphere. For all samples, the following procedure was used: samples were heated from 50 to 180 °C recorded the transition temperature. Then cold down to 50 °C, and then reheated to 180 °C, all at a rate of 10 °C/min. The recorded temperatures were calibrated using indium as standard. The T_g of star polymers measured at the second heating scan (Fig. 5) were lower than the counterparts based on the first heating scan (see Table. 1). This is reasonable because of the influence of the star polymers thermal history.

As reported in our earlier paper [26], only the linear PMPCS with $M_{n,GPC}$ beyond 10,200 g/mol could form liquid-crystalline phase. Wan et al. [25] also synthesized a series of MJLCPs (PMPCS) with a low polydispersity using TEMPO-mediated free radical polymerization, and found that some oligomers did not exhibit a liquid-crystalline phase. These phenomena of MJLCP are much different from that of conventional side chain and main chain liquid-crystalline polymers. It was interesting to consider what the effect of branching would have on the liquid crystalline state of PMPC. Would the branch point preclude alignment of polymer rod or affect the type of morphology observed for the four-arm PMPCS? To answer these questions the liquid crystalline state of the four-arm star PMPCS was studied. The liquid-crystalline behavior of four-arm star polymers was studied using DSC and a polarized optical microscope. The results show in Table 1. As report earlier, when heating the linear PMPCS polymers above 136 °C could observe birefringence by POM, the liquid crystalline behavior was dependent on the molecular weights of polymer, when the linear PMPCS with $M_{n,GPC}$ beyond 10,200 g/mol could form liquid-crystalline phase [26]. The star polymers are themotropic liquid crystals, when heated above the glass transition temperature of star-shaped PMPCS polymers at 139 °C and up, the liquid crystalline was not observable by POM had less than 3.68×10^4 g/mol of the star polymers of the $M_{n,GPC}$, the value $M_{n,GPC}$ of each arm of all the four-armed star shaped polymers are little lower than that of the linear MPCS polymer. The birefringence did not disappear until the decomposition temperature was reached, indicating a good stability of the liquid crystal phase of the polymers. This phenomenon has not yet been reported elsewhere to our knowledge, and detailed investigations are still underway.

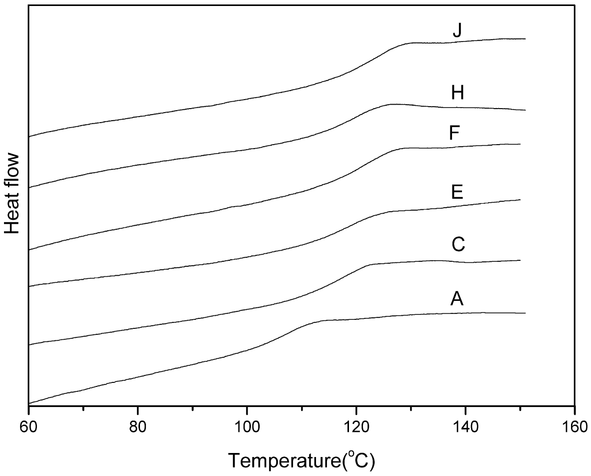


Fig. 5. DSC traces recorded during the second heating scan of four-armed star mesogen-jacketed liquid crystal polymers of different $M_{n,GPC}$: (A) $M_{n,GPC} = 0.84 \times 10^4$ g/mol. (C) $M_{n,GPC} = 3.09 \times 10^4$ g/mol, (E) $M_{n,GPC} = 4.73 \times 10^4$ g/mol, (F) $M_{n,GPC} = 5.36 \times 10^4$ g/mol, (H) $M_{n,GPC} = 6.50 \times 10^4$ g/mol, (J) $M_{n,GPC} = 7.71 \times 10^4$ g/mol.

It will be of interest to investigate the dilute-solution properties of the star liquid crystalline polymer and some applications (such as modifying on other material and as a stationary phase in liquid chromatography). The information obtained will be reported on in the near future. We expect that these studies will provide new insight into the polymer formation process.

4. Conclusion

Synthesis of four-arm star-shaped PMPCS with different molecular weight and low polydispersity was successfully achieved by ATRP in chlorobenzene solution using PT-Br as an initiator and CuBr/Sp complex as a catalyst. The ‘living’ ATRP of MPCS is verified by the following evidence first-order kinetics, a linear molecular weight-conversion profile and narrow molecular weight contribution ($M_w/M_n < 1.19$). The liquid-crystalline behavior of the star polymers with $M_{n,GPC}$ ranging from 0.84×10 to 7.71×10^4 g/mol was studied using DSC and POM. All polymers showed one glass transition, and T_g increased with increasing $M_{n,GPC}$ up to 3.68×10^4 g/mol, above which it became molecular weight independent. Only the star polymers with $M_{n,GPC}$ beyond 3.68×10^4 g/mol could form a liquid crystalline phase, which was found to be stable with a high clearing point.

Acknowledgements

The authors thank the Key Project of Young Teachers Scientific Research Funds of Hunan Provincial Education Department (02B07) for support of this work.

References

[1] Hawker CJ, Frechet JMJ. In: Ebdon JR, Eastmond GG, editors. New methods of polymer synthesis, vol. 2. New York: Chapman & Hall; 1995. p. 290.

[2] Mourey TH, Turner SR, Rubenstein M, Frechet JMJ, Hawker CJ, Wooley KL. Macromolecules 1992;25(9):2401–6.

[3] Hawker CJ, Farrington P, Mackay M, Frechet JMJ, Wooley KL. J Am Chem Soc 1995;117(15):4409–10.

[4] Jansen JF, Brabander van den Berg EM, Meijer EW. Science 1994; 266:1226–9.

[5] Fetters LJ, Kiss AD, Pearson DS, Quack GF, Vitus FJ. Macromolecules 1993;26(4):647–54.

[6] Simms JA, Spinelli HJ. In: Hatada K, Kitayama T, Vogl O, editors. Star polymer synthesis, vol. 40. New York: Marcel Dekker; 1997. p. 379.

[7] Schaefgen JR, Flory J. J Am Chem Soc 1948;70(8):2709–18.

[8] Morton M, Helminiak TD, Gadkary SD, Bueche F. J Polym Sci 1962; 57:471–82.

[9] Kanaoka S, Sawamoto M, Higashimura T. Macromolecules 1991; 24(9):2309–13.

[10] Zhang X, Xia J, Matyjaszewski K. Macromolecules 2000;33(7): 2340–5.

[11] Kennedy JP, Jacob S. Acc Chem Res 1998;31(12):341–835.

[12] Shohi H, Sawamoto M, Higashimura T. Macromol Chem 1992;193: 2027–31.

[13] Ohno K, Wong B, Haddleton DM. J Polym Sci 2001;39:2206–10.

[14] Davis K, Matyjaszewski K. Adv Polym Sci 2002;159:1–169.

[15] Xia J, Zhang X, Matyjaszewski K. Macromolecules 1999;32(13): 4482–4.

[16] Hawker CJ, Malmstrom EE, Frechet JMJ, Leduc MR, Grubbs RB, Barclay GG. In: Matyjaszewski K, editor. Design strategies for branched and highly branched macromolecular architectures using nitroxide-mediated living free-radical procedures. ACS symposium series, vol. 685. Washington, DC: American Chemical Society; 1998. p. 433.

[17] Otsu T, Matsumoto A. Adv Polym Sci 1998;136:75–137.

[18] Berge CT, Frgd M, Johnson JW, Moad G, Rizzardo E, Scopazzi C, Thang SH. PCT Int APPL WO2000002939, Al20000120; Chem Abstr, 1999; 132: 3843.

[19] Matyjaszewski K, Miller PJ, Pyun J, Kickelbick G, Diamanti S. Macromolecules 1999;32(20):6526–33.

[20] Veda J, Kamigaito M, Sawamoto M. Macromolecules 1998;31(20): 6762–8.

[21] Kasko AM, Heintz AM, Pugh C. Macromolecules 1998;31(2): 256–71.

[22] Angot S, Murthy S, Taton D, Gnanou Y. Macromolecules 1998;31(2): 7218–25.

[23] Hedrick JL, Trollsas M, Hawker CJ, Claesson AH, Heise A, Miller RD, Mecerreyes D, Jerome R, Dubois P. Macromolecules 1998; 31(25):8691–87065.

[24] Hawker CJ, Bosman AW, Harth E. Chem Rev 2001;101(2):3661–88.

[25] Wan XH, Tu HL, Zhou QF. Chin J Polym Sci 1999;17(2):189–92.

[26] Zhang H, Yu Z, Wan X, Zhou QF, Woo EM. Polymer 2002;43: 2357–61.

[27] Zhou QF, Wan XH, Zhang D, Feng XD. In: Isayev AI, Kyu T, Cheng SZD, editors. Liquid-crystalline polymer systems technological advances. ACS symposium series, vol. 632. Washington, DC: American Chemical Society; 1996. p. 344–57.

[28] Zhou QF, Wan XH, Zhu XL, Zhang F, Feng XD. Mol Cryst Liq Cryst 1993;231:107–17.

[29] Wan XH, Zhang F, Wu P, Feng XD, Zhou QF. Macromol Symp 1995; 96:207–18.

[30] Zhang D, Liu YX, Wan XH, Zhou QF. Macromolecules 1999;32(16): 5183–5.

[31] Zhou QF, Zhu XL, Wen ZQ. Macromolecules 1989;22(1):491–3.

[32] Matyjaszewski K, Coca S, Gaynor SG, Wei M, Woodworth BE. Macromolecules 1998;31(16):5967–9.

[33] Moineau G, Minet M, Dubois P, Teyssie P, Senniger T, Jerome R. Macromolecules 1999;32(1):27–35.