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Effects of molecular weight on liquid-crystalline behavior of a mesogen-jacketed liquid crystal polymer synthesized by atom transfer radical polymerization

H. Zhang, Z. Yu, X. Wan, Q.-F. Zhou*, E.M. Woo[1]

Department of Polymer Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

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Abstract

The synthesis of poly{2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene} (PMPCS) with different molecular weight and low polydispersity was achieved by atom transfer radical polymerization in methoxybenzene solution using 1-bromoethylbenzene as an initiator and CuBr/sparteine complex as a catalyst. The concentration of the living centers throughout the polymerization was found to be constant. The liquid-crystalline behavior of the polymers with M_n ranging from 3800 to 17,400 g/mol was studied using DSC and POM. Only the polymers with M_n beyond 10,200 g/mol formed a liquid-crystalline phase, which was quite stable with a high clearing point (higher than the decomposition temperature of the polymer). © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Atom transfer radical polymerization; Controlled radical polymerization; Liquid crystal polymer

1. Introduction

The mesogen-jacketed liquid-crystalline polymers (MJLCPs) in which the mesogenic units are laterally attached to the polymer main chain with or without short spacers have been attracting considerable attentions since Zhou et al. [1] first proposed the concept in 1987. Three series of MJLCPs based on 2-vinylhydroquinone (VHQ), 2-vinyl-1,4-phenylenediamine (VPDA) and 2-vinylterephthalic acid (VTA) were synthesized by conventional radical polymerization in recent years [2–6]. However, the conventional radical polymerization does have some disadvantages. It is difficult to synthesize MPLCPs with controlled molecular weight, low polydispersity and well-defined chain-ends by the conventional radical polymerization. To overcome these difficulties, Wan et al. [7,8] first synthesized a series of MJLCPs (poly{2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene} (PMPCS)) with low polydispersity and a series of novel rod–coil diblock copolymers with polystyrene and PMPCS using the 2,2,6,6-tetramethy-1-piperidinyl-oxy (TEMPO)-mediated free radical polymerization. Tu et al. [9] have studied the self-assembly of this copolymer. The results showed that the copolymer chains could self-assemble into a coil-shell nano-structure when a PS-b-PMPCS dilute solution was cooled down. Atom transfer radical polymerization (ATRP) [10,11], which has the merit of living/controlled radical polymerization, interests us. We have also noticed that Pugh et al. have synthesized linear and three-arm star side chain liquid-crystalline polymers by ATRP [12]. In this study, synthesis of PMPCS by ATRP was attempted by catalyzing with CuBr/sparteine (Sp), initiated by 1-bromoethylbenzene (BEB) in methoxybenzene (Scheme 1). The resulting polymers have a predictable molecular weight and a narrow molecular weight distribution.

In the past years, many researchers have focused their interests on the influence of molecular weight on the phase behavior of both side chain and main chain liquid-crystalline polymers [13–15]. The concept of 'MJLCPs' was proposed to describe the side chain liquid crystal polymers, which are of side chain type but with mesogenic units attached laterally to the main chain without spacers or with only relatively short spacers. This type of polymers is expected to have a stiff chain conformation because of the steric requirement of the rigid and bulky mesogenic units. This idea has been repeatedly supported by studies of, e.g. Hardouin [16], Gray [17], Richardson [18], Schrock [19],

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* Corresponding author.
E-mail address: qfzhou@pku.edu.cn (Q.-F. Zhou).

[1] Visiting from Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan.

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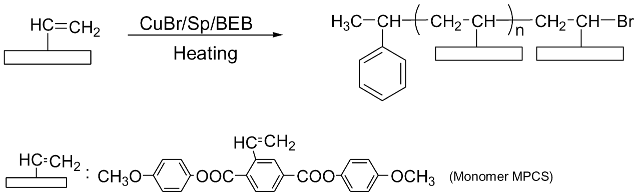

Scheme 1. Atom transfer radical polymerization of MPCPS.

Mauzac [20], Xu [21], Zhou [3–5,22], and most recently, Ober and coworkers [23]. However, the effects of molecular weight and polydispersity on the properties, including liquid crystallinity, were not well studied. In this paper, we have investigated the liquid-crystalline behavior of MPCS and PMPCS with M_n ranging from 3800 to 17,400 g/mol by using DSC and POM characterization. The effect of molecular weight on the liquid-crystalline behavior of MJLCPs is also first reported.

2. Experimental

2.1. Materials and procedures

2,5-Bis[4-methoxyphenyl]-oxycarbonyl)styrene (MPCS) was synthesized using the method of Zhang et al. [6] CuBr was prepared from $CuBr_2$ and purified by stirring in acetic acid, washing with methanol, and then dried in vacuum. Sp (Aldrich) was distilled under reduced pressure over calcium hydride and stored under a nitrogen atmosphere at 4 °C in the dark. BEB, also from Aldrich, was used without further purification. Methoxybenzene and tetrahydrofuran (THF) were used as received.

Typically, MPCS (0.808 g, 2.00 mmol), BEB (7.40 mg, 0.04 mmol), CuBr (5.74 mg, 0.04 mmol) and Sp (18.76 mg, 0.08 mmol), and methoxybenzene (0.808 g) were charged into a polymerization tube under ambient atmosphere. After being degassed with three freeze-thaw cycles, the tube was sealed off under vacuum. Subsequently, the tube was immersed into a thermostatted oil bath at a pre-set temperature. The tube was sampled at suitable time intervals during the reaction and quenched in cold THF to room temperature. The sample was further diluted with THF, and the mixture was then poured into a large volume of methanol to precipitate the polymer. The precipitate was washed thoroughly with methanol and dried in a vacuum oven overnight at room temperature. The conversion of polymerization was determined gravimetrically.

2.2. Measurements

Molecular weights M_n and polydispersity index ($\mathrm{PDI} = M_w/M_n$) were measured on a gel permeation chromatograph (Waters 150C) equipped with three Waters Styragel columns (10^3, 10^4, and 10^5 Å) using THF as an eluent phase at 35 °C. The column system was calibrated by a set of monodisperse standard polystyrenes. ^{1}H NMR spectra were obtained on a 200 Varian NMR instrument using $CDCl_3$ as solvent, tetramethylsilane (TMS) as the internal standard. DSC traces were obtained using a TA DSC 2010 instrument. Polarized optical microscope observation was performed on a Leitz Laborlux 12 POL microscope with a Leitz-350 hot stage.

3. Results and discussion

Complexation of Sp with CuBr in methoxybenzene can easily take place and a homogeneous solution could be achieved even at room temperature. MPCS also has good solubility in methoxybenzene. Thus, as MPCS, BEB, CuBr, Sp and methoxybenzene were charged into a polymerization tube, a bright yellow transparent solution was formed at elevated temperatures (>40 °C). As soon as the polymerization started, the reaction medium became red, and the reaction mixture remained in a homogeneous state during the progress of reactions.

The various results of polymerization of MPCS in methoxybenzene for various conditions are presented in Figs. 1–3. They are each discussed as following. Fig. 1 shows the linearity of the semi-logarithmic plot of $\ln([M]_0/[M])$ versus time, which indicates that the polymerization is first order with respect to the monomer concentration and that the living radical concentration is constant. An induction time was observed for the polymerization of MPCS in solution, particularly at lower temperatures. The reason is not clear at the present time, but it is speculated that the residual oxygen might be the cause of induction time [24]. However, the experiment was repeated several times and the observed induction time remained the same. An alternative explanation might be related to the formation of the actual initiating center as a result of the interaction between the catalyst complex and the initiator [25]. Sp can have two possible conformations: transoid or cisoid [26]. In the free state, it has the transoid structure, but when

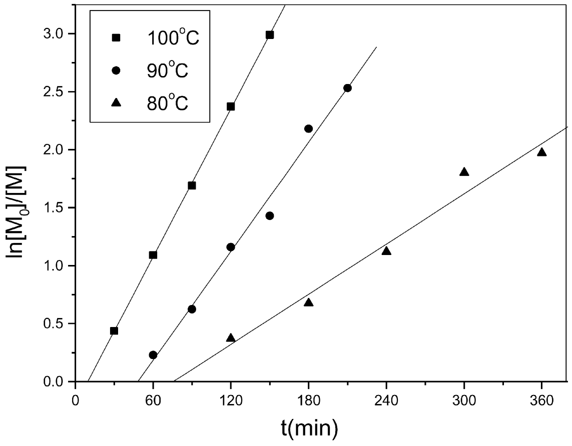

Fig. 1. Kinetic plots of polymerization of MPCS in methoxybenzene solution (50 wt%) at various temperatures. [MPCS]/[BEB]/[CuBr]/[Sp] = 50:1:1:2.

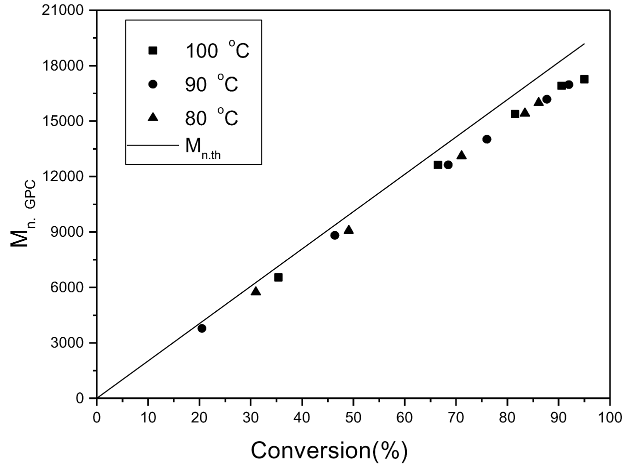

Fig. 2. Dependence of number-average molecular weight (M_n) on conversion of MPCS in methoxybenzene. Symbols same as in Fig. 1.

complexed with a metal ion, it acquires the cisoid shape. The formation of the actual initiating center might be associated with the conformation change. At higher temperatures, the formation of the actual initiating center is expected to be faster and this leads to a shorter induction time, which is in agreement with the experimental result of this study.

At 80 °C, styrene virtually does not polymerize under the stated experimental conditions of this study. By comparison, the polymerization rates of MPCS are faster than the rates of styrene at the same temperature as the conversion could reach 88.0% in 360 min at 80 °C. One explanation might be related to the substituent group effects. MPCS can be considered as a styrene substituted by two electron-withdrawing [(4-methoxy)phenyl]oxy-carbonyl groups at *ortho-* and *meta*-positions. The effect of the substituents on 'living' free radical polymerization based on TEMPO/BPO initiating system of styrene has been studied recently by Barclay, Kazmaier and others [27,28]. They found that electron-withdrawing substituents, such as CF_3 increased the rate of TEMPO-mediated living radical polymerization. Matyjaszewski et al. [29] have also showed that, in the ATRP, monomers with electron-withdrawing substituents result in better polymerization control and polymerize faster than those with electron-donating substituents. An alternative explanation on the enhanced polymerizability of MPCS might be related to the spatial orientation of the monomer molecules.

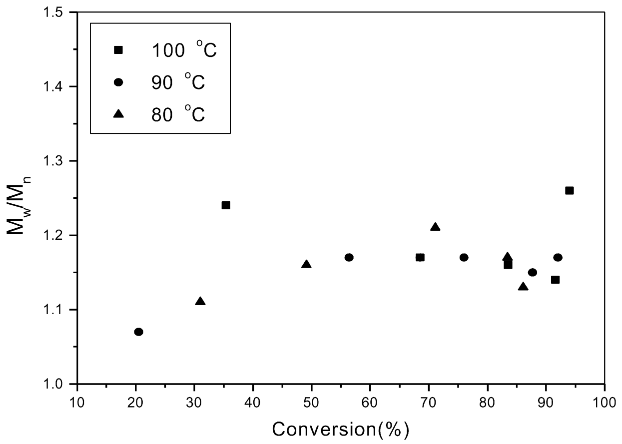

Fig. 3. The dependence of the polydispersity: M_w/M_n, on the monomer conversion of MPCS in methoxybenzene. Symbols same as in Fig. 1.

The M_n increased linearly with the conversion for the solution polymerization of the monomer, which is one of the indications of a living polymerization. However, Fig. 2 shows that the determined M_n of PMPCS was somewhat lower than the calculated value, probably because of the difference in hydrodynamic properties of PMPCS and PS, the latter was used as the standard in molecular weight measurements. A qualitative explanation for this finding is to be seen in the much large mass per unit length of MJLCPs than the calibration standard PS. The true molar mass should therefore be higher than the GPC molar mass. There is, however, an opposing effect that has to do with the stiffening of the polymer chain imposed by the spatially demanding substituents. This leads to an increased hydrodynamic volume, causing the GPC molar mass to become larger than the actual molar mass. For the cases shown in Fig. 2 the latter effect obviously does not overcompensate the former. Fig. 3 shows that, throughout the polymerization of MPCS the PDI remained quite low (<1.3), which is another characteristic feature of a living polymerization.

Because it is a chiral ligand, Sp was generally used for the control of the stereochemistry of organic reactions or of asymmetric polymerization. In addition, Sp possesses a chiral cavity, therefore the corresponding reaction can occur asymmetrically [30]. In addition, since MPCS has a rigid and bulky side group, it would ensure a much stable helical conformation. One of our original objectives of this work is to synthesize a novel one hand helical conformation MJLCP by ATRP. However, Fig. 4 shows that the ^1H NMR spectrum of PMPCS obtained in the presence of Sp was just similar to that obtained by conventional radical

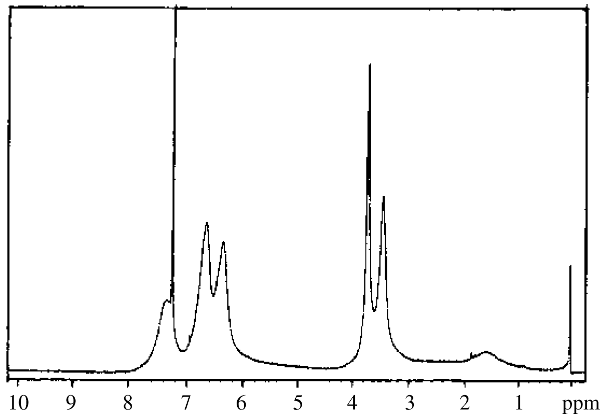

Fig. 4. ^1H NMR spectrum of PMPCS with $M_n = 5700$ g/mol.

Table 1
Properties of polymer with different molecular weight

Polymers	$M_n \times 10^{-4}$	M_w/M_n	T_g (°C)	Liquid crystallinity	T^* (POM, °C)[a]	Clearing point (°C)
1	0.38	1.07	109.8	No	–	–
2	0.57	1.07	113.8	No	–	–
3	0.65	1.24	116.1	No	–	–
4	0.88	1.17	119.7	No	–	–
5	0.91	1.16	120.1	No	–	–
6	1.02	1.23	120.7	Yes	~136	> 350
7	1.11	1.13	121.1	Yes	~136	> 350
8	1.40	1.17	120.7	Yes	~136	> 350
9	1.62	1.15	120.6	Yes	~136	> 350
10	1.74	1.17	120.0	Yes	~136	> 350

[a] The temperature at which the birefringence develops noticeably, which may be higher than T_g.

polymerization and nitroxide-mediated living free radical polymerization [7,8]. The expected resonance for the main chain protons and the end-group –CHBr proton is weak in the spectrum of PMPCS. Armes and coworkers [31] examined the temperature-induced micellization of a zwitterionic copolymer of 2-(dimethylamino) ethylmethacrylate-block-methacrylic acid (DMAEMA-block-MAA) using ^{1}H NMR spectroscopy. They have found that the intensities of the NMR signals decreased significantly as the hydrophobic DMAEMA block forms a micelle core at elevated temperatures. Accordingly, the earlier mentioned fact may be due to reduced solvation and mobility of the main chain, the result of the 'mesogen-jacket' effect. Even though the end-group –CHBr cannot be verified using ^{1}H NMR, these polymers could initiate styrene or MMA by ATRP to obtain block copolymers (work to be reported in future papers). The optical activity of the polymer was also measured and found that $[\alpha]_{365}$ equal to zero ($c = 40$ mg/2 ml, THF). One hand helical conformation MJLCP was not achieved by ATRP.

We have investigated the liquid-crystalline behavior of MPCS and PMPCS with M_n ranging from 3800 to 17,400 g/mol by using DSC and POM characterization. The results are shown in Table 1. The monomer MPCS could form a liquid-crystalline phase upon melting, while all of synthesized polymers showed only one single glass transition. In addition, their T_g shifted to higher temperatures with increasing M_n up to 8800 g/mol, above which they became molecular weight independent. Only the polymers with M_n beyond 10,200 g/mol (or DP = 25) could form liquid-crystalline phase at 136 °C and up. Wan et al. [7] also synthesized a series of MJLCPs (PMPCS) with a low polydispersity using the 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. So far, there is a general agreement that the number and nature (i.e. virtual, monotropic, or enantiotropic) of phase transition were determined by a combination of thermodynamic and kinetic factors. Since the rate of formation of highly ordered phases (crystalline and smectic) decreases with increasing polymer molecular weight, the number and nature of the liquid-crystalline phases exhibited by the liquid-crystalline polymers varies with increasing molecular weight according to the following trend: monotropic nematic, enantiotropic nematic and enantiotropic smectic, enantiotropic nematic and monotropic smectic, enantiotropic nematic [13]. An increase of the polymer molecular weight increases mesomorphic–mesomorphic and mesomorphic–isotropic phase transition temperatures up to a certain degree of polymerization, above which they become molecular weight independent. Our results show the nature of the phases exhibited by MJLCP varies with increasing molecular weight according to the following trend: amorphism, nematic. These results also supported the Zhou's postulated model [1] that for the MJLCPs, with mesogenic units laterally attached via no spacers to main chain, the mesophase is formed by polymer chains as a whole and not only by the mesogenic units as for most conventional (end-on) side-chain polymers in which the main chains usually take a random coil conformation as described by the oblate NI phase proposed by Wang and Warner [32].

4. Conclusion

Synthesis of PMPCS with different molecular weight and low polydispersity was successfully achieved by ATRP in methoxybenzene solution using BEB as an initiator and CuBr/Sp complex as a catalyst. Plots of $\ln([M]_0/[M])$ versus time and molecular weight versus monomer conversion exhibited linear dependence, which indicated that the concentration of the living centers throughout polymerization was constant. An induction time was observed during the solution polymerization.

The liquid-crystalline behavior of the polymers with M_n ranging from 3800 to 17,400 g/mol was studied using DSC and POM. All polymers showed one glass transition, and T_g increased with increasing M_n up to 8800 g/mol, above which it became molecular weight independent. Only the polymers with M_n beyond 10,200 g/mol could form a liquid-crystalline phase, which was found to be stable with a high clearing point (higher than decomposition temperature of the polymer).

Acknowledgements

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