

Rapid Communications

**NITROXIDE-MEDIATED FREE RADICAL SYNTHESIS OF
MESOGEN-JACKETED LIQUID CRYSTAL POLYMERS***

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Abstract The first TEMPO-mediated “living” free radical polymerization of liquid crystalline monomer, 2, 5-bis[(4-methoxyphenyl)oxycarbonyl]styrene (MPCS), was carried out at 130 °C with BPO as an initiator. The molecular weight of the polymer can be varied from rather low values to high values while maintaining narrow polydispersity. It was observed that the polymerization of MPCS proceeded much faster than that of styrene. A tentative explanation for this fast polymerization was suggested.

Keywords TEMPO, “Living” free radical polymerization, Mesogen-jacketed liquid crystal polymer, Mesophase polymerization

Living polymerization has been attracting considerable attentions from both academic and industrial researchers since Szwarc^[1] first proposed the concept in 1956. The main interest of these studies is to synthesize macromolecules with complex and controlled architectures such as block copolymers, graft copolymers, ladder polymers, star polymers and dendrimers^[2]. However, conventional anionic and cationic living polymerizations do have some disadvantages. The active species tend to attack the polar functional groups and only a rather limited number of monomers can be used. In addition, they require either ultra-pure solvents and reagents or rigorous exclusion of oxygen and water^[3]. To overcome these difficulties, a lot of efforts have been focused on “living”/controlled free radical polymerization which can be carried out under mild, synthetically nondemanding reaction conditions^[4-7]. Among many techniques, the polymerization of styrene mediated by a stable nitroxide like 2, 2, 6, 6-tetramethyl-1-piperidinyl-oxy (TEMPO) is most extensively studied. According to Georges^[8], this “living” free radical polymerization proceeds *via* the reversible capping of growing chain ends with TEMPO, which reduces the free radical concentration and thus the occurrence of side reactions.

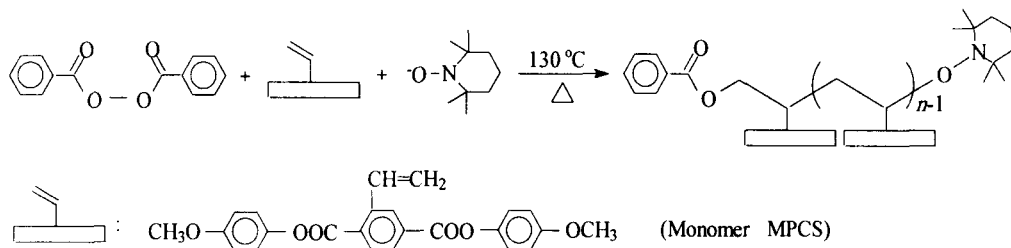
The present study investigates the TEMPO-mediated free radical polymerization of 2, 5-

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bis[(4-methoxyphenyl)oxycarbonyl]styrene (MPCS), a novel monomer which is different from previously studied monomers in that it has a rigid and bulky mesogenic unit as the pendent group. To date little research has addressed the effect of monomer orientation on "living" free radical polymerization, thus this work may also provide the first example of the TEMPO-mediated "living" free radical polymerization carried out in a mesophase.



Scheme 1 TEMPO-mediated free radical polymerization of MPCS

MPCS was synthesized by using a method described elsewhere^[9]. The polymerization process is illustrated in Scheme 1. Typically, 200 mg of MPCS, 1.2 mg of BPO and 1.0 mg of TEMPO were charged into a polymerization tube containing 1.15 mL (none if in bulk) of chlorobenzene. After being degassed with three freeze-thaw cycles, the tube was sealed off under vacuum. The reaction mixture was heated at 90 °C for 3 h to make BPO decompose completely and then at 130 °C for a predetermined duration allowing the polymerization to proceed. Then the mixture was cooled to room temperature. Polymers were obtained by precipitation with methanol followed by filtration. Percentage conversions were calculated from the weight of the polymers. Molecular weights were measured on a Waters 150C gel permeation chromatograph equipped with three Waters Styragel columns (10², 10³ and 10⁴ nm respectively) using tetrahydrofuran as the eluent at room temperature. The column system was calibrated by a set of standard monodisperse polystyrenes.

The effect of TEMPO on the polymerization of MPCS was first examined by varying the TEMPO/BPO molar ratio. As can be seen from Fig. 1, the monomer conversion at a fixed polymerization time decreases with increasing the [TEMPO]/[BPO] ratio. There is also an obvious trend that the polydispersity decreases as the [TEMPO]/[BPO] ratio increases. However, the polydispersity seems to level off at high [TEMPO]/[BPO] ratios. The similar behavior was observed for the bulk polymerization (not shown). The significant decrease in polydispersity might be explained by a mechanism of the living free radical polymerization of styrene^[5].

As the monomer conversion and the polydispersity are both not influenced by the TEMPO/BPO ratio, if the ratio is around 1.3 or larger, the TEMPO/BPO ratio was fixed at 1.3 in the following reactions.

In order to study the molecular weight change with conversion, the polymerization of MPCS was stopped at various reaction time intervals. In Fig. 2, the average molecular weight (M_n) and polydispersity of poly[2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene] (PMPCS) are plotted against the monomer conversion. In general, M_n increases linearly with conversion during the primary stage, which is one of the indications of living polymerization. Furthermore, a narrow polydispersity was maintained to be lower than the theoretical limit of 1.5 for conventional free radical polymerization at relatively lower monomer conversions, which is the another characteristic feature of living polymerization. The results suggest that this polymerization system possesses the "living" character to a certain extent. It is perhaps worth noting that there is a slight broadening of molecular weight distribution with increasing conversion. This may be due to the complex series of initiating steps of the TEMPO/BPO

bimolecular initiator systems, which have been shown to result in a variety of side reactions leading to the loss of initiator efficiency^[4, 10]

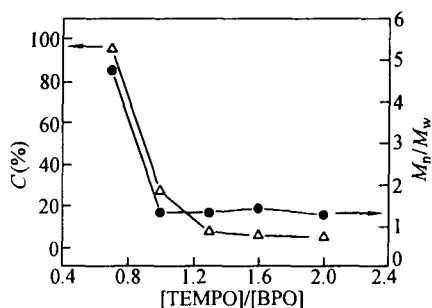


Fig. 1 Effect of the [TEMPO]/[BPO] ratio on the polymerization rate and polydispersity of PMPCS

Polymerizations were carried out with [MPCS]=0.43 mol/L and [MPCS]/[BPO]=100 in chlorobenzene at 130°C for 40 h

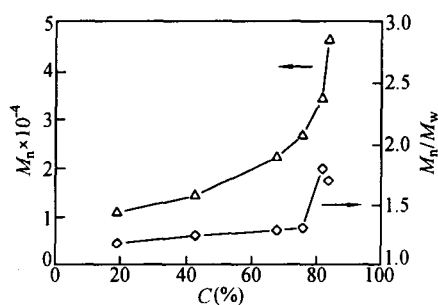


Fig. 2 Plot of the number-average molecular weight (M_n) and polydispersity of PMPCS against the conversion of the monomer. Reaction temperature: 130°C, [MPCS]:[TEMPO]:[BPO] = 100:1.3:1, in bulk

Table 1. TEMPO-mediated free radical polymerization of MPCS and styrene*

Monomer	<i>t</i> (h)	M_n	M_w/M_n	<i>C</i> (%)
MPCS	0.67	22066	1.28	68
Styrene	16	6151	1.22	56
	24	8108	1.24	71

* [monomer]:[TEMPO]:[BPO] = 100:1.3:1; reaction temperature: 130°C, in bulk

MPCS can be considered as a styrene substituted by two [(4-methoxy)phenyl]oxy-carbonyl groups at ortho and meta positions, respectively. The effect of substituents on "living" free radical polymerization of styrene has been studied recently by Barclay, Kazmaier and others^[10, 11]. They found that electron-withdrawing substituents, such as the CF₃- and the acetoxy group, would increase the rate of TEMPO-mediated living free radical polymerization. For comparison, TEMPO-mediated free radical polymerizations of MPCS and styrene were carried out at the same condition (Table 1). To our surprise, the polymerization of MPCS is not only much faster than that of styrene, but also faster than those functionalized styrenes with CF₃- or acetoxy groups, although MPCS has a rigid and bulky side group and thereafter would endure much higher steric hindrance with polymerization. So, the enhanced polymerizability of MPCS cannot be explained from the point of view of electric or steric efforts. MPCS is a thermotropic liquid crystalline monomer. It melts into a nematic phase at 109°C which persists up to a temperature of 144°C before the isotropic liquid is formed. So the sharp increase of the polymerization rate may be rationalized by the spatial orientation of the monomer molecules. Certainly, there is a lot of work to be done before any reliable conclusion can be made.

REFERENCES

- 1 Szwarc, M., Levy, M. and Milkovich, R., J. Am. Chem. Soc., 1956, 78: 2656
- 2 Webster, O.W., Science, 1991, 251: 887
- 3 Hawker, C.J., Acc. Chem. Res., 1997, 30: 373

- 4 Moad, G., Rizzardo, E. and Solomon, D.H., *Macromolecules*, 1982, 15: 909
- 5 Georges, M.K., Veregin, R.P.N., Kazmaier, P.M. and Hamer, G.K., *Macromolecules*, 1993, 26: 2987
- 6 Wang, J.S. and Matyjaszewski, K., *Macromolecules*, 1995, 28: 7901
- 7 Percec, V. and Barboiu, B., *Macromolecules*, 1995, 28: 7970
- 8 Georges, M.K., Veregin, R.P.N., Kazmaier, P.M. and Hamer, G.K., *Trends Polym. Sci.*, 1994, 2: 66
- 9 Liu, Y.X., Zhang, D., Wan, X.H. and Zhou, Q.F., *Chinese J. Polym. Sci.*, 1998, 16(3): 283
- 10 Barclay, G.G., Hawker, C.J., Ito, H., Orellana, A., Malenfant, P.R.L. and Sinta, D.F., *Macromolecules*, 1998, 31: 1024
- 11 Kazmaier, P.M., Daimon, K., Georges, M.K. and Gordon, K.H., *Polym. Prepr.*, 1996, 37: 485