

“LIVING” FREE RADICAL SYNTHESIS OF NOVEL ROD COIL DIBLOCK COPOLYMERS WITH POLYSTYRENE AND MESOGEN-JACKETED LIQUID CRYSTAL POLYMER SEGMENTS*

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Abstract The synthesis of rod-coil diblock copolymers was achieved for the first time by TEMPO-mediated “living” free radical polymerization of styrene and 2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene(MPCS). The block architecture of the two diblock copolymers thus prepared, MPCS-b-St(5400/2400) and MPCS-b-St(10800/8700), was confirmed by GPC, DSC studies and the formation of multimolecular micelles.

Keywords TEMPO; “Living” free radical polymerization; Rodcoil diblock copolymer; Mesogen-jacketed liquid crystal polymer

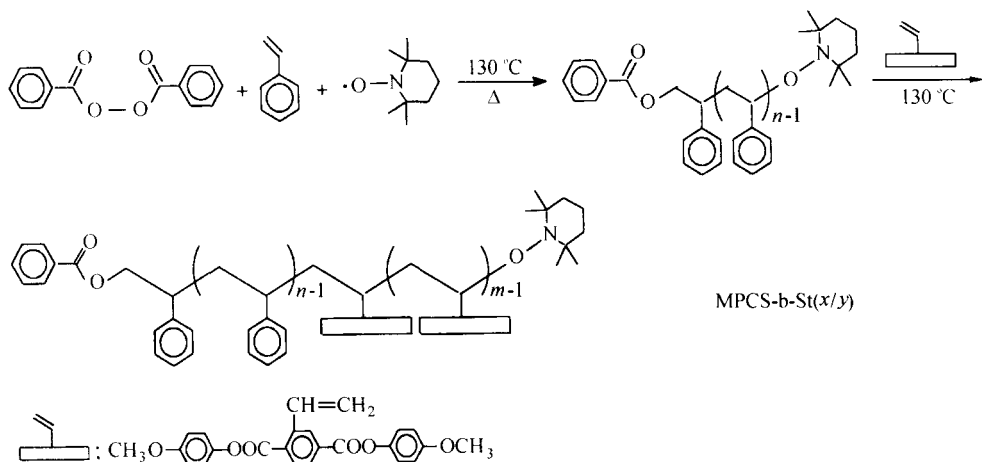
AB diblock copolymers consisting of a flexible coil block and a rigid rod block are a kind of fascinating self-assembling materials^[1]. Most of the rodcoil diblock copolymers were synthesized by living anionic and/or cationic polymerization to meet the requirements of narrow-polydispersity, controlled molecular weight and well-defined chain ends^[2]. However, anionic and cationic polymerization do have shortcomings as the active species react with functional groups severely and only a rather limited choice of monomers can be used^[3]. In recent years, much work has focused on 2,2,6,6-tetramethyl-1-piperidinyloxy(TEMPO)-mediated “living” free radical polymerization^[4,5]. Unlike living anionic and cationic polymerization, this technique does not require ultrapure solvents and reagents. Significantly, the vinyl monomers with functional groups can also be polymerized using this method. In this study, we report on the TEMPO-mediated “living” free radical synthesis and some properties of polystyrene-block-poly{2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene},

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hereafter designated as MPCS-*b*-St(*x/y*), where *x* is the M_n of the poly{2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene}(PMPCS) block and *y* is the M_n of the polystyrene(PSt) block. PMPCS is a new mesogen-jacketed liquid crystal polymer with mesogenic units attached directly to the main chain at the waist or gravity position^[6]. To the best of our knowledge, MPCS-*b*-St(*x/y*) is the first liquid crystal-coil diblock copolymer prepared by TEMPO-mediated “living” free radical polymerization.

GPC data were collected on a Waters 150C Gel Permeation Chromatography (Waters Styragel column 10², 10³, 10⁴ nm) using THF as eluent and monodisperse standard polystyrene for calibration. Thermograms were obtained using a TA DSC 2010 instrument. Polarized optical microscopy observation was performed on a Leitz Laborlux 12 Pol microscopy with Leitz 350 hot stage.



Scheme 1 Synthetic route of MPCS-*b*-St(*x/y*)

MPCS was synthesized using the method as described previously^[7]. MPCS-*b*-St(*x/y*) was prepared by sequential copolymerization of styrene and MPCS (scheme 1). Typically, a solution of styrene (12 mL, 100 mmol), BPO (0.209 g, 1 mmol) and TEMPO (0.161 g, 1.3 mmol) was charged into a polymerization tube. 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 at 130°C for predetermined time allowing the polymerization to proceed, then cooled to room temperature. PSt-TEMPO adduct was precipitated from methanol and dried in vacuum oven overnight. Two diblock copolymers, MPCS-*b*-St (5400/2400) and MPCS-*b*-St (10800/8700), were synthesized using two PSt-TEMPO adducts as initiators in this preliminary communication (Table 1). Considering the rather high melting point of MPCS (108~109°C) and probably bad solubility of PSt-TEMPO in MPCS and relatively less amount of reagents used, which all mean

difficulty for PSt-TEMPO to be dispersed homogeneously in MPCS melt at polymerization temperature, the chain extension was finished in p-xylene. During the polymerization, the reaction mixture kept clear and colorless all the time. Upon being cooled to room temperature, a somewhat cloudy but homogeneous solution formed. Because p-xylene can dissolve PSt but not PMPCS, this should suggest the formation of multimolecular micelles. The micellization in a selective solvent is characteristic of block copolymers but not of pure random copolymers nor of polymer mixtures^[8], this behavior may have indirectly confirmed the diblock architecture of MPCS-b-St(*x/y*). However, a further verification of this diblock nature was carried out by GPC and DSC as is described below.

Table 1 GPC, DSC, TGA data and liquid crystallinity of MPCS-b-St(*x/y*)

Copolymer	$M_n \times 10^{-3}$	M_w/M_n	T_g (°C)	T_d (°C)*	LC phase
PSt-TEMPO (I)	2.40	1.13			
MPCS-b-St(5400/2400)	7.80	1.43	89.5 110.0	333.0	nematic
PSt-TEMPO(II)	8.70	1.25	89.6	300.0	
MPCS-b-St(10800/8700)	19.5	1.48	93.2 117.3	326.5	nematic
PMPCS	20.0	2.50	117.5	354.8	nematic

*: 1% weight loss

Fig. 1 shows the GPC spectra of MPCS-b-St(10800/8700) and PSt-TEMPO(II). Obviously, the GPC curve of PSt-TEMPO shifts left after being reacted with MPCS. The polydispersity of copolymer is a little higher than its predecessor due to the much longer polymerization time, but still lower than theoretical limit ($M_w/M_n = 1.5$) of conventional free radical polymerization. This is also the case of MPCS-b-St(5400/2400). It is noted that a very small shoulder peak at the position of PSt-TEMPO can be seen for both copolymers. According to Fukuda^[8], some of polystyrene (less than 5%) may be not capped by TEMPO in the chain ends. These inactive polystyrene will not initiate MPCS to polymerize when heated with MPCS at 130°C and should remain in the copolymer if no special precaution was paid to separate them. Therefore, the shoulder peak should correspond to the TEMPO free polystyrene. In order to prove this, the as-obtained MPCS-b-St was extracted with cyclohexane and subjected to GPC measurement again. Because cyclohexane can dissolve PSt but not MPCS-b-St, only should pure MPCS-b-St remain in the resulted sample. As shown in Fig. 1, the shoulder peak of pure PSt in MPCS-b-St(10800/8700) disappeared after being extracted with cyclohexane.

The glass transition temperature (T_g) of pure PMPCS and PSt-TEMPO are 117.5°C and 89.6°C, respectively. The two distinct glass transitions are observed in

diblock copolymers. For MPCSt-b-St(10800/8700), the first takes place at 93.2°C, corresponding to the glass transition of the PSt block and the second at 117.2°C, corresponding to that of PMPCSt. This may be another evidence of block structure of MPCSt-b-St.

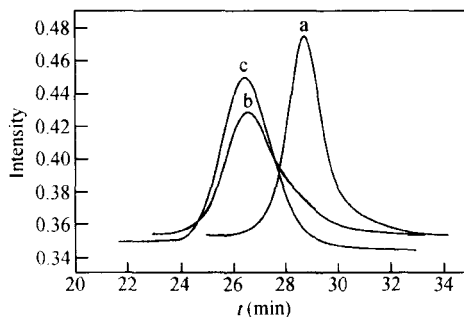


Fig. 1 GPC traces of PSt-TEMPO(II) and MPCSt-b-St(10800/8700).

a: PSt-TEMPO(II); b: MPCSt-b-St(10800/8700, as obtained); c: MPCSt-b-St(10800/8700, after extraction)

PMPCSt represents one of the novel type side chain liquid crystal polymers, the mesogen-jacketed liquid crystal polymers(MJLCPs). Early studies on lyotropic behavior, banded texture and solution properties have proved the rodlike nature of MJLCPs^[9,10]. It is expected that such a rodcoil diblock copolymer with a polystyrene block and a MJLCPs block will have unique supermolecular structure and self-assembly behavior. Detailed investigations are under way.

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