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Ersin I. Serhatli ^a, Giancarlo Galli ^b, Yusuf Yagci ^c, Michele Laus ^d, Sante A. Angeloni ^e & Emo Chiellini ^f

^a Department of Chemistry and Industrial Chemistry, University of Pisa, 56126 Pisa, Italy, Department of Chemistry, Istanbul Technical University 80626 Istanbul, Turkey

^b Department of Chemistry and Industrial Chemistry, University of Pisa, 56126 Pisa, Italy

^c Department of Chemistry, Istanbul Technical University 80626 Istanbul, Turkey

^d Department of Industrial Chemistry and Materials Chemistry, University of Bologna, 40136 Bologna, Italy

^e Department of Industrial Chemistry and Materials Chemistry, University of Bologna, 40136 Bologna, Italy

^f Department of Chemistry and Industrial Chemistry, University of Pisa, 56126 Pisa, Italy

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Synthesis of liquid crystalline graft and block copolymers by sequential cationic and free-radical polymerizations

ERSIN I. SERHATLI^{1,2}, GIANCARLO GALLI^{1,*}, YUSUF YAGCI², MICHELE LAUS³, SANTE A. ANGELONI³ and EMO CHIellini^{1,*}

¹ *Department of Chemistry and Industrial Chemistry, University of Pisa, 56126 Pisa, Italy*

² *Department of Chemistry, Istanbul Technical University, 80626 Istanbul, Turkey*

³ *Department of Industrial Chemistry and Materials Chemistry, University of Bologna, 40136 Bologna, Italy*

Abstract—New graft and block copolymers were synthesized by two procedures, each consisting of a sequence of cationic and free-radical polymerization reactions. One polymer component was a liquid crystalline side-group polymer, with the other polymer component being incorporated in crystalline grafts or in amorphous blocks. The copolymers were microphase-separated and underwent thermal transitions (glass, melting, isotropization) of each individual component.

Keywords: Liquid crystals; graft copolymers; block copolymers.

1. INTRODUCTION

The macromolecular engineering of graft and block copolymers via various synthetic routes has resulted in the realization of very diverse copolymer structures [1]. These systems are able to microphase-separate in ordered morphologies, because of the incompatibility of the different polymer segments [2]. In particular, when a polymer component shows liquid crystalline (LC) properties, the order at molecular level (LC order) as well as at supramolecular level (phase morphology) can be studied in a single copolymer structure [3]. Furthermore, phase-separated polymer systems with an LC side-group polymer can have advanced applications, e.g. in electro-optics [4–6]. While LC block copolymers have attracted much attention [7–9], comparatively very little work has been done on LC graft copolymers [10–13].

*To whom correspondence should be addressed. E-mail: gallig@dcc.unipi.it, chlmeo@dcc.unipi.it

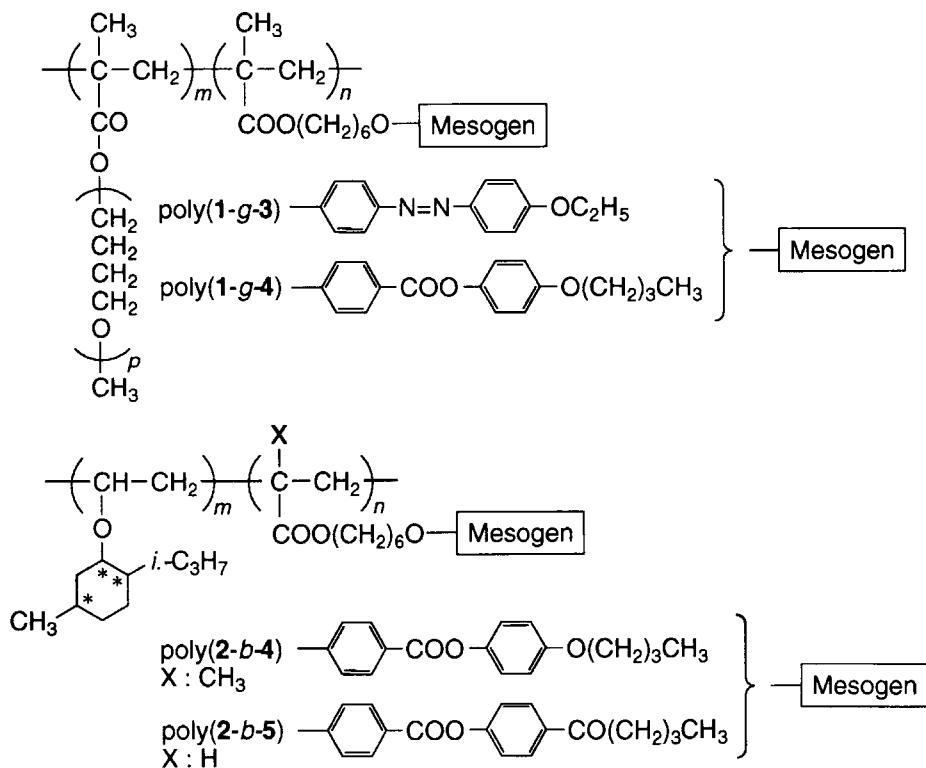


Figure 1. Simplified structures of the graft and block copolymers synthesized.

In this paper we describe our synthetic approach to engineering new graft copolymers poly(1-g-3) and poly(1-g-4) and block copolymers poly(2-b-4) and poly(2-b-5) containing LC polymer segments (Fig. 1). The former polymers consisted of a polymer backbone derived from an LC side-group monomer, either **3** or **4**, bearing crystalline polymer grafts from tetrahydrofuran (**1**); the latter systems comprised blocks from an LC side-group monomer, either **4** or **5**, and amorphous chiral polymer blocks from menthyl vinyl ether (**2**).

2. EXPERIMENTAL

2.1. Synthesis

Full details on the synthesis of LC monomers **3–5** will be given elsewhere [14]. **2** ($[\alpha]_D^{25} = -73^\circ$ (neat)) was synthesized following a literature procedure [15].

2.1.1. Preparation of 9. 100 ml (1.24 mol) of **1** was distilled under argon into a reaction flask that had previously been dried at 130°C under vacuum overnight. 0.14 ml (1.24 mmol) of **6** was injected with a syringe and the polymerization was allowed to proceed at 25°C for 45 min. 0.5 ml (5.7 mmol) of **8** was then added and

the reaction mixture was precipitated into water at 5°C. The polymer was filtered and dried under vacuum. Yield 72% ($M_n = 7000$ and $M_w/M_n = 1.20$, by SEC).

2.1.2. Preparation of macromonomer 11. 10 ml (11 mmol) of a 1.1 M solution of **10** in water was added dropwise to a solution of 0.5 g (0.07 mmol) of **9** in 10 ml of tetrahydrofuran at -2°C . The mixture was stirred for 1 h at -2°C and allowed to stand overnight. The solution was concentrated to a small volume under vacuum and the resulting precipitate was filtered and dried. Yield 85% ($M_n \approx 7200$, $DP_n \approx 100$, $M_w/M_n = 1.24$, by SEC).

$^1\text{H-NMR}$ (CDCl_3) $\delta = 2.56$ (m, 4H, CH_2), 3.38 (m, 4H, OCH_2). The signals of the methacrylic ester moiety at 6.1 and 5.5 ($\text{CH}_2=$), 4.2 (COOCH_2), and 2.0 (CH_3) could not be integrated because of their extremely low intensity.

2.1.3. Preparation of poly(1-g-3). 0.15 g (0.021 mmol of methacrylate group) of **11** and 0.15 g (0.37 mmol) of **3** were dissolved in 5 ml of dry benzene with 9 mg (0.05 mmol) of AIBN. After repeated freeze–thaw degassing cycles, the polymerization was allowed to proceed for 4 days at 70°C . The polymer was precipitated into methanol, filtered, and purified by extraction in a Kumagawa extractor with boiling ethanol. Yield 44%.

2.1.4. Preparation of 14. 0.07 g (0.22 mmol) of **12** and 0.12 g (0.44 mmol) of **13** were dissolved in 50 ml (0.24 mol) of **2** at room temperature under dry nitrogen. After 15 min, the reaction mixture was filtered and the polymer was precipitated in methanol, filtered, and purified by repeated precipitations from chloroform into ethanol. Yield 75% ($M_n \approx 12000$, $DP_n \approx 70$, $M_w/M_n = 2.3$, by SEC). $[\alpha]_D^{25} = -186^\circ$ (chloroform).

$^1\text{H-NMR}$ (CDCl_3) $\delta = 0.45$ – 1.20 (m, 15H, aliphatic), 1.20– 1.85 (m, 3H, CHC(O)CH_2), 1.90– 2.35 (m, 2H, backbone CH_2), 2.95– 3.80 (m, 2H, CHOCH). The signals of the azo-cyanopentanoyl moiety could not be detected.

2.1.5. Preparation of poly(2-b-4). 0.07 g (5.8×10^{-3} mmol of azo group) of **14** and 0.60 g (1.32 mmol) of **4** were dissolved in 5 ml of dry tetrahydrofuran. After repeated freeze–thaw degassing cycles, the polymerization was allowed to proceed for 3 days at 80°C . The polymer was precipitated into methanol, filtered, and purified by extraction in a Kumagawa extractor with boiling *n*-heptane. Yield 58%. $[\alpha]_D^{25} = -76^\circ$ (chloroform).

2.2. Characterization

$^1\text{H-NMR}$ spectra were recorded with a Varian XL300 spectrometer operating at 300 MHz. Size exclusion chromatography (SEC) measurements were carried out with a Perkin-Elmer 2/2 chromatograph equipped with Shodex A802/S and A803/S columns using UV and RI detectors. Monodisperse polystyrene samples

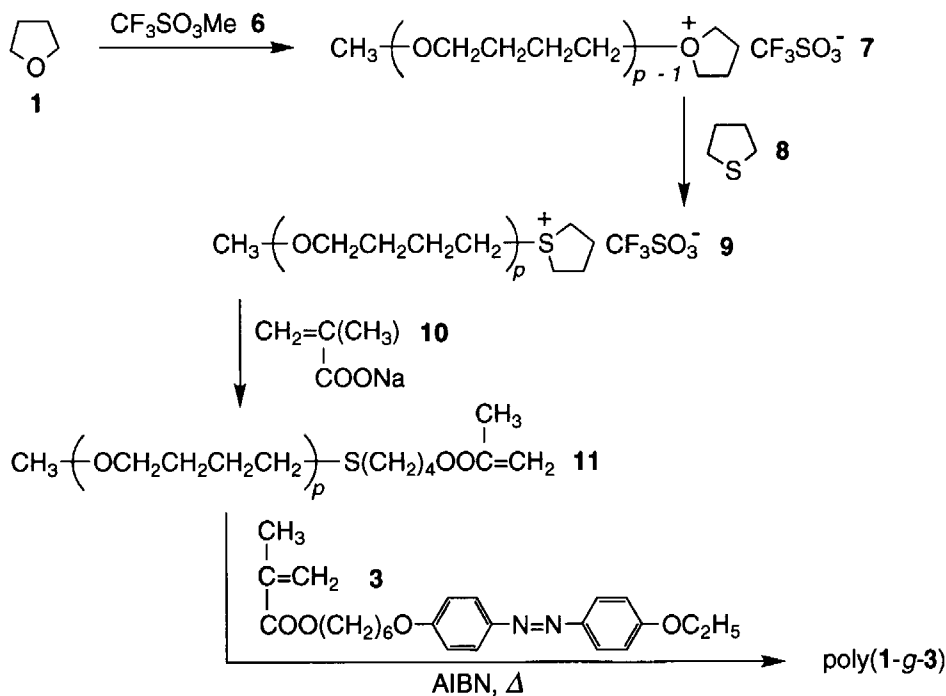
were used for calibration. The temperatures of glass transition (T_g), melting (T_m), and mesophase-isotropic or isotropization (T_i) were detected by differential scanning calorimetry at $10^\circ\text{C}/\text{min}$ scanning rate. The transition enthalpies (ΔH_m , ΔH_i) were evaluated using indium calibration.

3. RESULTS AND DISCUSSION

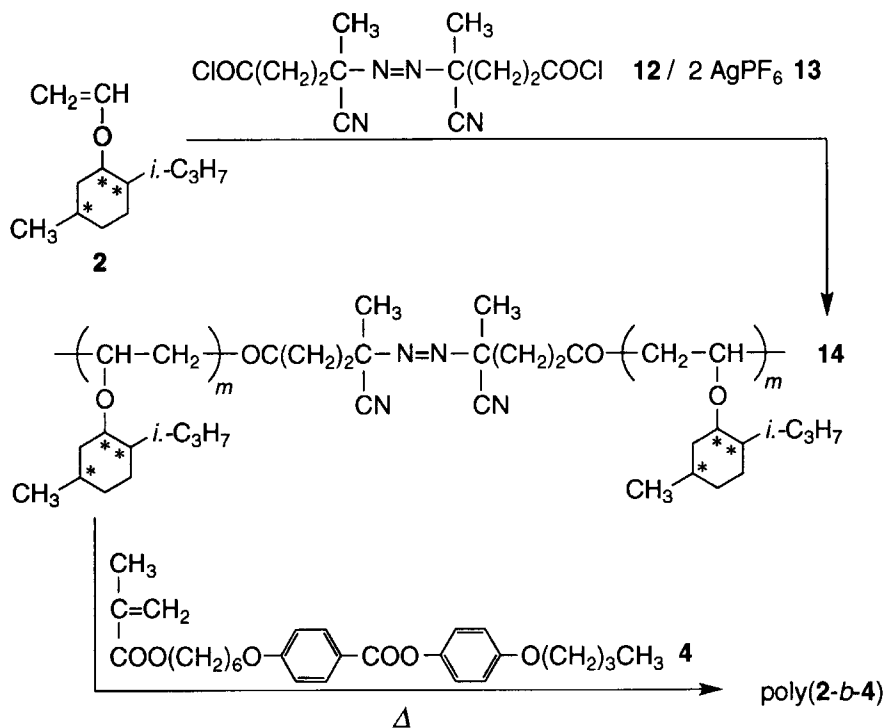
In general, LC graft copolymers and block copolymers were prepared by two-step procedures, each involving a sequence of cationic and free-radical polymerization reactions, as exemplified in Schemes 1 and 2, respectively.

According to the first procedure (Scheme 1), tetrahydrofuran (**1**) was polymerized using methyl triflate (**6**) as a cationic initiator to produce polymer **7**, which was end-capped by treating it with tetrahydrothiophene (**8**). The resulting thiolanium salt **9** was isolated and then modified with sodium methacrylate (**10**), which yielded methacrylate-terminated poly(tetrahydrofuran) **11** [16]. Finally, this macromonomer was copolymerized free radically in the presence of AIBN with the LC side-chain monomer **3**, or **4**, forming graft copolymer poly(**1-g-3**), or poly(**1-g-4**). The copolymers were purified by extraction with boiling ethanol, in which poly(**1**) homopolymer is selectively soluble.

Following the second procedure (Scheme 2), menthyl vinyl ether (**2**) was polymerized with the azo-bis(4-cyanopentanoyl chloride) (**12**)/silver hexafluorophosphate



Scheme 1.



Scheme 2.

(**13**) (1 : 2 by mol) cationic system, thus giving the poly(menthyl vinyl ether) homopolymer **14** that contained one central thermally labile azo group in the polymer chain. This macroinitiator was then used to initiate the free-radical polymerization of the LC side-chain monomer **4**, or **5**, which yielded block copolymer poly(2-b-4), or poly(2-b-5). While the former was of the AB type, the latter was of the ABA type, the block from **2** being the A block, consistent with the preferred termination mechanism of the LC methacrylate **4** (disproportionation) and of the acrylate **5** (combination) [17, 18]. These copolymers were purified by extraction with boiling *n*-heptane, which is a selective solvent for poly(**2**) homopolymer.

The formation of copolymers was confirmed by SEC. The SEC curves exhibited distributions of the molecular weights in which the polymer species were uniformly distributed (Fig. 2).

The composition and average degree of polymerization of the copolymers were evaluated by $^1\text{H-NMR}$. Starting with macromonomer **11**, graft copolymers poly(1-g-3) and poly(1-g-4) with 5 and 15 wt% of units from **1** were obtained, corresponding to an average number of 330 and 90 units of the LC monomers **3** and **4** per graft from **1**, respectively. Using macroinitiator **14**, block copolymers poly(2-b-4) and poly(2-b-5) with 50 wt% of units from **2** were prepared, corresponding to $DP_n \approx 15$ and 30 of the LC monomers **4** and **5**, respectively. Therefore, this synthetic approach allowed the preparation of copolymers with various molecular

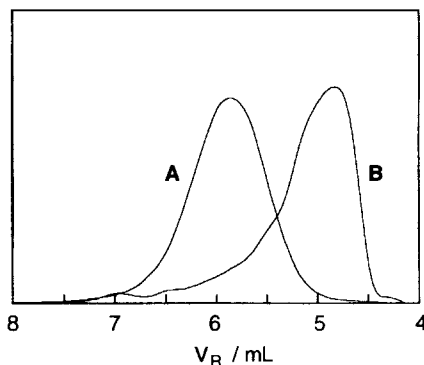


Figure 2. SEC curves of macromonomer **11** (A) and graft copolymer poly(**1-g-3**) (B) therefrom.

weights and contents of the polymer components. Different block copolymer structures were also obtained.

Both graft and block copolymers formed thermotropic mesophase(s), the nature of which evidently depended on the structure of the LC polymer component, in close analogy to their respective LC homopolymers. The mesophase behavior of the copolymers will be described in detail in a following paper [14]. For example, poly(**2-b-5**) presented $T_g = 42^\circ\text{C}$ for block **2** and $T_g = 3^\circ\text{C}$ and $T_i = 147^\circ\text{C}$ ($\Delta H_i = 11.1 \text{ J/g}$) for block **5**; poly(**1-g-3**) exhibited $T_m = 28^\circ\text{C}$ ($\Delta H_m = 20 \text{ J/g}$) for graft **1** and $T_g = 55^\circ\text{C}$ and $T_i = 132^\circ\text{C}$ ($\Delta H_i \approx 1 \text{ J/g}$) for component **3**. These findings clearly showed that the copolymers were phase-separated in the melt phase, due to the incompatibility of the different components, and underwent their individual phase transitions. This behavior was independent of the architecture of the copolymers and of the crystalline or amorphous character of the other non-LC polymer component that did not prevent the mesogenic segments from segregating and ordering in LC domains.

In conclusion, by sequential cationic and free-radical polymerization reactions it was possible to prepare graft and block copolymers that incorporated an LC constituent and either crystalline grafts or amorphous blocks. Each copolymer exhibited LC thermotropic behavior because of microphase separation of the chemically different polymer components. The adopted procedures are versatile and may permit the production of a great variety of structures of LC copolymers.

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