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Molecular engineering of liquid crystalline polymers by living polymerization

21. Synthesis and characterization of poly{3-[(4-cyano-4'-biphenyl)oxy]propyl vinyl ether} macromonomers*

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SUMMARY

This paper describes the synthesis and characterization of poly{3-[4-cyano-4'-biphenyl)oxy]propyl vinyl ether} [poly(6-3)] macromonomers obtained by the functionalization of the growing chain end of the corresponding living polymer obtained by the initiation of the cationic polymerization of 3-[4-cyano-4'-biphenyl)oxy]propyl vinyl ether with $CF_3SO_3H/S(CH_3)_2$, with 2-hydroxy ethyl methacrylate [poly(6-3)-I], 2-[2-(2-allyloxyethoxy)ethoxy]ethanol [poly(6-3)-II] and 10-undecen-1-ol [poly(6-3)-III].

INTRODUCTION

In recent years there has been much interest in the cationic polymerization of mesogenic vinyl ethers because it can be performed under living polymerization conditions.[1-4] Living polymerization allows the control of several important primary parameters for the synthesis of well defined polymer structures such as molecular weight, molecular weight distribution and chain end functional groups.[5] These properly tailored macromolecules can then be used to design new polymeric materials. Macromonomers can be synthesized by either initiating a living polymerization with a functional initiator or terminating it with a compound that contains the appropriate functional group.

Up to now, we have investigated the influence of molecular weight on the phase transitions of poly{ω-[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether}s (6-n) (where n represents the number of methylenic groups in the flexible spacer) with alkyl groups from ethyl to undecanyl.[6] These living polymerization experiments also allowed us to investigate the influence of composition on the phase behavior of binary copolymers at constant molecular weight.[7] In addition, we have demonstrated that a quantitative functionalization of the chain ends of poly(6-10)[8] is possible with the initiating system $CF_3SO_3H/S(CH_3)_2$ in CH_2Cl_2.[9] Additional functionalization reactions of the living chain ends derived from the cationic polymerization of alkyl vinyl ethers were reported.[10]

This paper will describe the synthesis of poly{3-[4-cyano-4'-biphenyl)oxy]propyl vinyl ether} [poly(6-3)] macromonomers by end capping the corresponding living polymer with 2-hydroxy ethyl methacrylate, 2-[2-(2-allyloxyethoxy)ethoxy]ethanol and 10-undecen-1-ol.

EXPERIMENTAL

Scheme I outlines the synthesis of poly(6-3) macromonomers.

Materials

All materials were commercially available and were used as received or purified as described previously.[6] 2-Hydroxyethyl methacrylate (98%, Aldrich), triethylene glycol (anhydrous, >97%, Fluka), allyl chloride (98%, Aldrich), 10-undecenoic acid (99%, Aldrich) and 2,6-lutidine (99%, Aldrich) were used as received. Methyl sulfide (anhydrous, 99%, Aldrich) was refluxed over 9-borabicyclo[3.3.1]nonane (9-BBN, crystalline, 98%, Aldrich)

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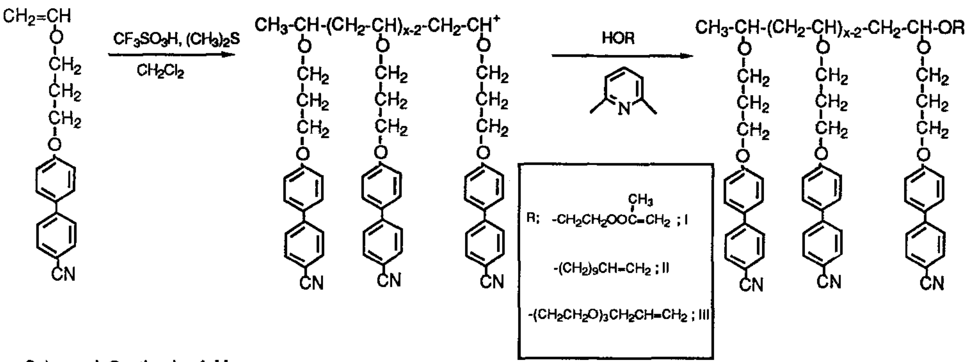

Scheme I. Synthesis of Macromonomers

and then distilled under argon. Dichloromethane (99.6%, Aldrich) used as a polymerization solvent was first washed with concentrated sulfuric acid, then with water, dried over anhydrous magnesium sulfate, refluxed over calcium hydride and freshly distilled under argon before each use. Trifluoromethane sulfonic acid (triflic acid, 98%, Aldrich) was distilled under argon.

Techniques

^{1}H-NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. TMS was used as internal standard. A Perkin Elmer DSC-4 differential scanning calorimeter, equipped with a TADS 3600 data station was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic and exothermic peaks respectively. In all cases, heating and cooling rates were 20°C/min unless otherwise specified. Glass transition temperatures (Tg) were read at the middle of the change in the heat capacity. For certain polymer samples, the first heating scans sometimes differ from the second and subsequent heating scans. At the proper place, this difference will be mentioned. However, the second and subsequent heating scans are identical. The first heating scans can be reobtained after proper thermal treatment of the polymer sample. Both the first and the second DSC heating scans will be reported and discussed. A Carl-Zeiss optical polarized microscope (magnification: 100x) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transitions and to analyze the anisotropic textures. Relative molecular weights were determined by gel permeation chromatography (GPC) with a Perkin Elmer series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler and a Nelson analytical 900 series integrator data station. The measurements were made at 40°C using the UV detector. A set of Perkin Elmer PL gel columns of 10^4 and 500 Å with $CHCl_3$ as solvent (1ml/min) and a calibration plot constructed with polystyrene standards was used to determine the molecular weights. Therefore, all molecular weights discussed in this paper are relative to polystyrene. High pressure liquid chromatography (HPLC) experiments were performed with the same instrument.

Synthesis of Monomers

3-[(4-Cyano-4'-biphenyl)oxy]propyl vinyl ether (6-3) with a purity higher than 99% (HPLC) was synthesized according to a previous publication.[6b]

Synthesis of 10-Undecen-1-ol

10-Undecen-1-ol was synthesized by the reduction of 10-undecenoic acid with $LiAlH_4$ in dry THF and was purified by vacuum distillation (bp 132-133°C/15mm).[11]

Synthesis of 2-[2-(2-Allyloxyethoxy)ethoxy]ethanol

2-[2-(2-Allyloxyethoxy)ethoxy]ethanol was synthesized according to a modified literature procedure.[12] Its detailed synthesis and characterization will be described elsewhere.[13]

Polymerizations

Polymerizations were carried out in glass flasks equipped with teflon stopcocks and rubber septa under argon atmosphere at 0°C for 40 min. All glassware was dried overnight at 180°C. The 3-[4-cyano-4'-biphenyl)oxy]propyl vinyl ether (6-3) (0.4 g, 1.43 mmol) was further dried under vacuum overnight in the polymerization flask. After the flask was filled with argon, freshly distilled dry methylene chloride (4 ml) was added through a syringe and the solution was cooled to 0°C. Dimethyl sulfide (0.18 ml, 2.4 mmol) and triflic acid (21μl, 0.24 mmol) were then added via a syringe. After 40 min, 0.3 ml (2.4 mmol) of 2-hydroxy ethyl methacrylate was added followed by 0.1 ml of 2,6-lutidine. The cooling bath was removed and the mixture was allowed to warm up to room temperature. After 1 hr, the reaction mixture was precipitated into methanol. The filtered polymer was dried and precipitated from methylene chloride solution into methanol. The polymerization results are summarized in Table 1.

RESULTS AND DISCUSSIONS

3-[4-Cyano-4'-biphenyl]propyl vinyl ether (6-3) was polymerized by initiation with $CF_3SO_3H/S(CH_3)_2$ in methylene chloride at 0°C. After 40 min a hydroxy end capping agent containing a double bond and 2,6-lutidine as proton scavenger were introduced into the solution to quench the polymerization. The reaction scheme is outlined in Scheme I. Figure 1 shows GPC traces of poly(6-3)s containing various end groups. These polymers show a very narrow molecular weight distributions and their molecular weights can be controlled by the ratio of $[M]_0/[I]_0$ (Table 1). The end group structure of these polymers was determined by ^{1}H-NMR. Figure 2 shows the ^{1}H-NMR spectrum of 2-hydroxy ethyl methacrylate terminated poly(6-3) [poly(6-3)-I], Figure 3 presents the ^{1}H-NMR spectrum of 10-undecene-1-ol terminated poly(6-3) [poly(6-3)-II] and Figure 4 displays the ^{1}H-NMR spectrum of 2-[2-(2-allyloxyethoxy)ethoxy]ethanol terminated poly(6-3) [poly(6-3)-III]. The assignment of

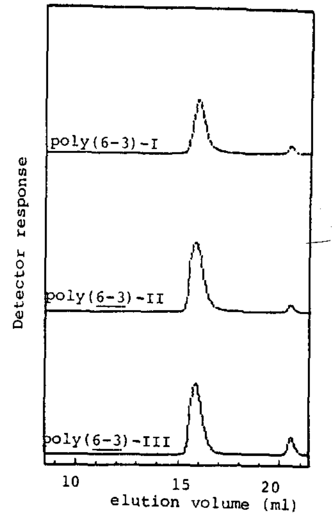

Figure 1. GPC traces of (A) poly(6-3)-I, (B) poly(6-3)-II and (C) poly(6-3)-III

Table 1. Synthesis of Poly{3-[(4-Cyano-4'-biphenyl)oxy]propyl Vinyl Ether} Macromonomers

Sample No.	$[M]_0/[I]_0$	end capping agent	yield (%)	Mn theor.	Mn (GPC)	Mw/Mn (GPC)	integration ratio p/k	DP (NMR)	Functionality
1	6.0	I	82	1790	1600	1.09	1.92	5.5	0.96
2	6.0	II	80	1830	1800	1.11	2.08	5.2	1.04
3	6.0	III	78	1940	1800	1.13	2.06	6.8	1.03

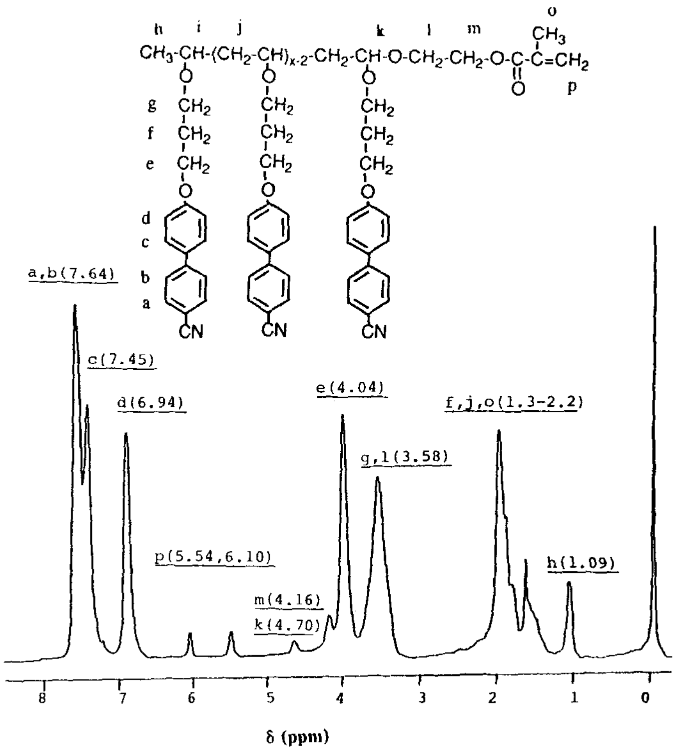

Figure 2. 200 MHz ^{1}H-NMR spectrum of poly(6-3)-I.

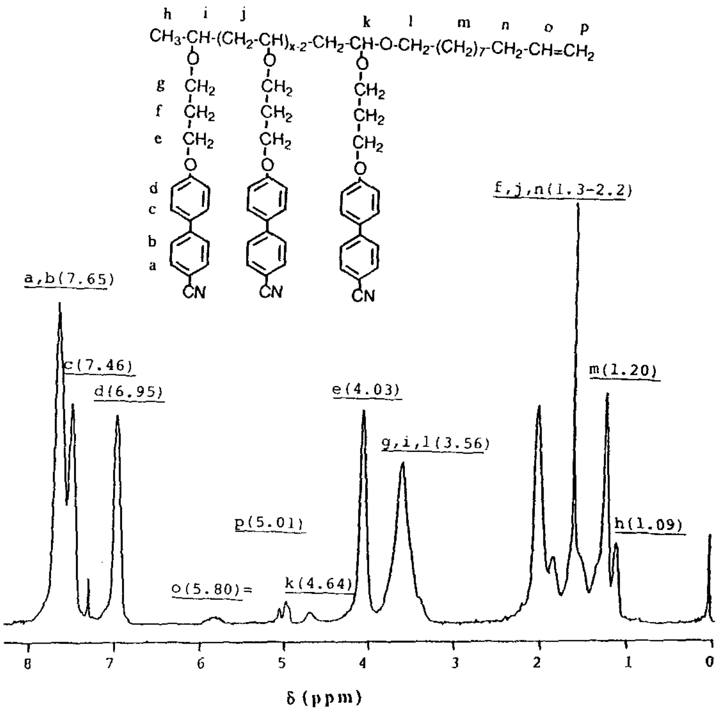

Figure 3. 200 MHz ^{1}H-NMR spectrum of poly(6-3)-II.

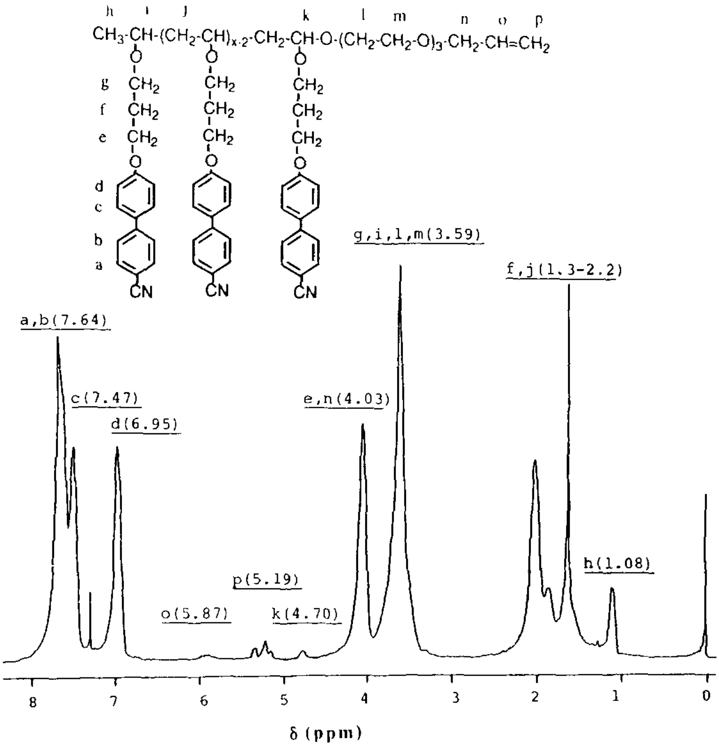

Figure 4. 200 MHz ^{1}H-NMR spectrum of poly(6-3)-III.

protonic resonances are also provided on these figures. The resonances of the expected unsaturated end-groups which are formed by quenching the living chain end with these three end capping agents can be easily observed in all cases. In addition, end capping with hydroxy groups lead to acetal containing end groups which are characterized as signal k (Figures 2,3,4). The signals due to aromatic proton (signal d) and acetal proton (signal k) were integrated. The calculated degrees of polymerization are close to the theoretical one, i.e., $[M]_0/[I]_0=6.0$. The number of functional end-groups in each polymer chain was determined by measuring the integral ratio between the resonances which are corresponded to $=C\underline{H_2}$ (signal p) and acetal proton (signal k), (Table 1). According to the NMR spectrum, the polymer chains are quantitatively end capped with an unsaturated functional group. These results demonstrate that the initiating system $CF_3SO_3H/(CH_3)_2S$ allows the preparation of poly(6-3) with well defined functional chain-ends.

The thermal characterization of poly(6-3) macromonomers by DSC is presented in Figure 5. All these macromonomers exhibit an enantiotropic nematic mesophase (Table 2, Figure 5). The thermal behavior of the macromonomers is similar to that of poly(6-3).[6] However, the phase transition temperatures of poly(6-3)-II and III decrease by comparison to that of poly(6-3).

In conclusion, these experiments have demonstrated that the initiating system $CF_3SO_3H/(CH_3)S$ can be used in the synthesis of mesogenic macromonomers.

Table 2. Thermal Transitions and Their Corresponding Thermodynamic Parameters of the Macromonomers of Poly(6-3)

Macromonomer	phase transitions (°C) and corresponding enthalpy changes (kcal/mru)	
	heating	cooling
poly(6-3)-I	g 36.2 X 42.5 (0.23) n 81.1 (0.076) i g 35.9 n 80.4 (0.081) i	i 75.7 (0.089) n 24.9 g
poly(6-3)-II	g 33.5 X 38.3 (0.17) n 71.6 (0.082) i g 32.0 n 71.4 (0.090) i	i 66.6 (0.088) n 25.8 g
poly(6-3)-III	g 25.8 X 33.6 (0.074) n 59.1 (0.055) i g 26.9 n 58.9 (0.066) i	i 53.0 (0.085) n 22.7 g

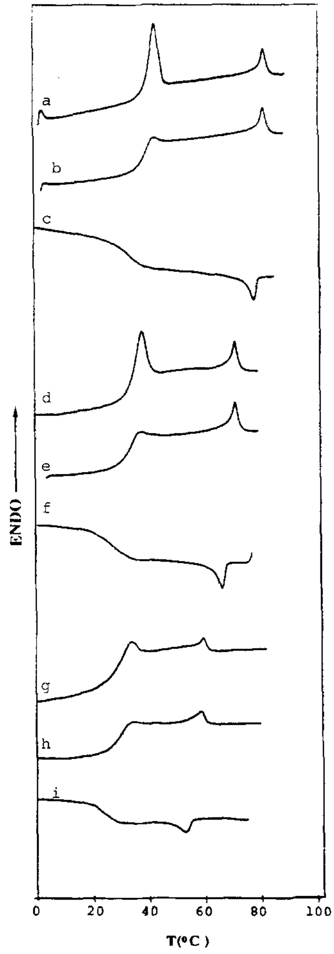

Figure 5. The DSC scans (20 °C/min) of poly(6-3)-I: (a) first heating scan, (b) second heating scan, (c) first cooling scan; of poly(6-3)-II: (d) first heating scan, (e) second heating scan, (f) first cooling scan: and of poly(6-3)-III: (d) first heating scan, (e) second heating scan, (f) first cooling scan

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