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Molecular engineering of liquid crystal polymers by living polymerization

6. Influence of molecular weight on the phase transitions of a 1/1 copolymer of 2-[(4-cyano-4′-biphenyl)oxy]ethyl vinyl ether and 8-[(4-cyano-4′-biphenyl)oxy]octyl vinyl ether

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SUMMARY

A 1/1 molar ratio of 2-[4-cyano-4'-biphenyl)oxy]ethyl vinyl ether (6-2) and 8-[(4-cyano-4'-biphenyl)oxy]octyl vinyl ether (6-8) was cationically copolymerized with the initiating system $CF_3SO_3H/(CH_3)_2S$ in methylene chloride at 0°C. All copolymers present narrow molecular weight distributions, and number average molecular weights which exhibit a linear dependence on $[M]_o/[I]_o$. Copolymers with degrees of polymerization lower than 14 exhibit an enantiotrpic nematic mesophase regardless of the thermal history of the sample. Copolymers with higher molecular weights exhibit an inverse monotropic smectic-A and an enantiotropic nematic mesophase in the first heating scan and only an enantiotropic nematic mesophase in the subsequent heating scans.

INTRODUCTION

Previous publications from this series have demonstrated that group transfer polymerization of mesogenic methacrylates[1] and cationic polymerization of mesogenic vinyl ethers[2-5] provide the most reliable synthetic methods which lead to living polymerization of mesogenic monomers. Our prefered initiating system for the cationic polymerization of mesogenic vinyl ethers is $CF_3SO_3H/(CH_3)_2S$.[6] Living cationic polymerization of mesogenic vinyl ethers was also accomplished by Sagane and Lenz.[7] Alternative methods which are used to synthesize side chain liquid crystalline polymers with narrow molecular weight distribution are based on polymer modification reactions[8]. We have also developed a novel method for the synthesis of the mesogenic vinyl ethers.[2-5] This allows the preparation of monomers with flexible spacers of various length. Previously the preparation of mesogenic vinyl ethers with only two methylenic units in the flexible spacer was readily accomplished[9]. We have also demonstrated that $CF_3SO_3H/(CH_3)_2S$ initiating system can be used for the cyclopolymerization and cyclocopolymerization of various functional monomers.[10,11] The goal of this paper is to describe the living cationic copolymerization of a 1/1 molar ratio of 2-[4-cyano-4'-biphenyl)oxy]ethyl vinyl ether (6-2) and 8-[(4-cyano-4'-biphenyl)oxy]octyl vinyl ether (6-8) and to describe the phase behavior of the resulting copolymer.

EXPERIMENTAL

Scheme I outlines the synthesis of the copolymer.

Materials

2-[4-Cyano-4'-biphenyl)oxy]ethyl vinyl ether (6-2)[5] and 8-[4-cyano-4'-biphenyl)oxy]octyl vinyl ether (6-8)[3] of higher purities than 99.9% were synthesized and characterized as described previously.

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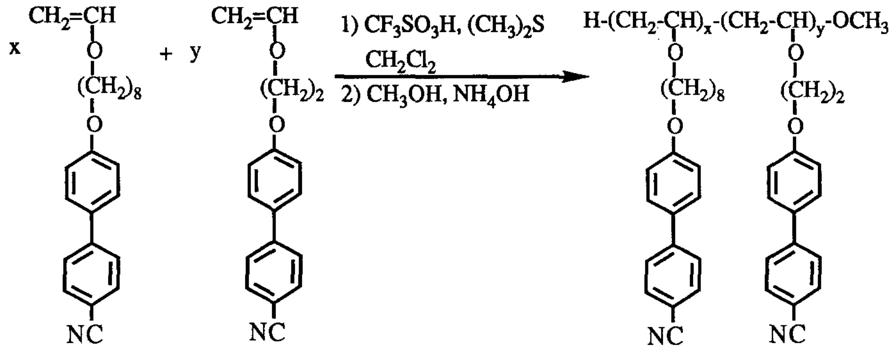

Scheme I
Synthesis of poly(6-8-co-6-2)1/1

Methyl sulfide (anhydrous, 99%, Aldrich) was refluxed over 9-borabicyclo[3,3,1]nonane (9-BBN dimer, crystalline, 98%, Aldrich) 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 $MgSO_4$, refluxed over calcium hydride and freshly distilled under argon before each use. Trifluoromethane sulfonic acid (triflic acid, 98%, Aldrich) was distilled under vacuum.

Techniques

200 MHz ^1H-NMR spectra was recorded on a Varian XL-200 spectrometer. A Perkin Elmer DSC-4 differential scanning calorimeter, equipped with a TADS data station was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic or exothermic peaks respectively. Heating and cooling rates were 20°C/min. Glass transition temperatures were read at the middle of the change in the heat capacity. In certain cases first heating scans differ from second and subsequent heating scans. However second and subsequent heating scans are identical. A Carl-Zeiss optical polarized microscope (magnification: 100x) equipped with a Mettler FP 82 hot stage and a Mettler 80 central processor was used to observe the thermal transitions and to analyze the anisotropic textures. 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 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.

Cationic polymerizations

Cationic polymerizations were performed in glass flasks equipped with teflon stopcocks and rubber septa under argon atmosphere at 0°C for 1 hr. All glassware was dried overnight at 130°C. The monomer was further dried under vacuum overnight in the polymerization flask. Then the flask was filled with argon, cooled to 0°C, and the requested amounts of methylene chloride, dimethyl sulfide and triflic acid were added via a syringe. The monomer concentration was about 10 wt% from the volume of solvent and the dimethyl sulfide concentration was 10 times larger than that of the initiator. The polymer molecular weight was controlled by $[M]_o/[I]_o$ ratio. At the end of the polymerization the reaction mixture was precipitated from methylene chloride solution into methanol containing few drops of NH_4OH. The filtered polymers were dried and reprecipitated from methylene chloride solution into methanol until GPC curves showed no traces of unreacted monomer. In all cases monomer conversions were higher than

99%. The reported yield are much lower than conversions due to polymer losses. Table I summarizes the polymerization results.

RESULTS AND DISCUSSION

The influence of molecular weight on the phase transitions of poly(6-8) was discussed in a previous publication from our laboratory[3], while that of poly(6-2) in a publication by Sagane and Lenz[7c]. The influence of copolymer composition on the phase behavior of poly(6-2-co-6-8) with a degree of polymerization of 10 was presented elsewhere[5]. Poly (6-2-co-6-8) with a molar ratio of 6-2 to 6-8 equal to 1/1, i.e, poly(6-2-co-6-8)1/1 and a degree of polymerization equal to 10 exhibits an enantiotropic nematic mesophase. The phase behavior of both poly(6-8) and poly(6-2) are molecular weight dependent.[3,7a] For example at low degrees of polymerization poly(6-8) displays enantiotropic smetic-A (s_A) and nematic (n) phases, at intermediary molecular weights an enantiotropic s_A phase, while at high molecular weights enantiotropic s_A and s_X phases. The phase behavior of poly(6-2-co-6-8) is determined by both the phase behavior of the parent homopolymers and by copolymer composition. Since the phase behavior of poly(6-2) and poly(6-8) is molecular weight dependent, we assume that the phase behavior of the copolymers should be both composition and molecular weight dependent. Table I summarizes the copolymerization results. Copolymerization of a 1/1 molar ratio of 6-2 to 6-8 led always to a 1/1 copolymer (tested by ^{1}H-NMR characterization of copolymers). The molecular weight of the copolymers was varied by changing the $[M]_o/[I]_o$ ratio. All copolymers have a narrow molecular weight distribution (Table I). Figure I plots the dependence of Mn on $[M]_o/[I]_o$ and the dependence of Mw/Mn on Mn. Both dependences demonstrate that these copolymerizations follow a living polymerization mechanism.

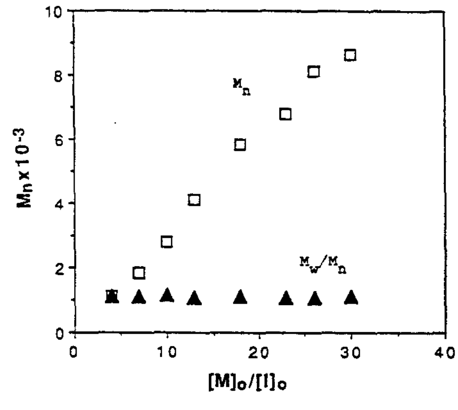

Figure 1: The dependence of the number average molecular weight (Mn) and of the polydispersity (Mw/Mn) of poly(6-2-co-6-8)1/1 on the $[M]_o/[I]_o$ ratio.

Figure 2a presents the first heating scans of the DSC curves of poly(6-2-co-6-8)1/1 with different degrees of polymerization. Second heating scans are presented in Figure 2b, while cooling scans in Figure 2c. The copolymers with degrees of polymerization lower than 18.9 exhibit an enantiotropic nematic mesophase. The coplymers with higher degrees of polymerization display an enantiotropic nematic and a monotropic s_A phase. The last one appears only in the first heating scan. Second heating and cooling scans show only an enantiotropic nematic mesophase regardless of the degree of polymerization of poly(6-2-co-6-8)1/1.

Table I. Cationic Polymerization of 6-2 with 6-8 (polymerization temperature, 0°C; polymerization solvent, CH_2Cl_2; $[M]o=[6\text{-}8+6\text{-}2]=0.325M$; $[6\text{-}8]/[6\text{-}2]=1$; $[(CH_3)_2S]_o/[I]_o=10$; polymerization time, 1hr) and Characterization of the Resulting Copolymers.

Sample no.	$[M]_o/[I]_o$	Polymer yield(%)	GPC			phase transitions (°C) and corresponding enthalpy changes (kcal/mru)	
			$Mn \times 10^{-3}$	Mw/Mn	DP	heating	cooling
1	4.0	71.0	1.10	1.10	3.60	g 19.2 n 93.3 (0.12) i g 18.1 n 93.8 (0.13) i	i 89.5 (0.14) n 11.3 g
2	7.0	63.9	1.86	1.10	6.10	g 23.1 n 97.2 (0.12) i g 22.3 n 96.6 (0.12) i	i 93.1 (0.14) n 14.0 g
3	10.0	61.8	2.82	1.17	9.20	g 33.7 n 102.0 (0.092) i g 31.5 n 101.9 (0.098) i	i 98.7 (0.11) n 22.4 g
4	13.0	61.8	4.11	1.08	13.40	g 38.7 n 107.5 (0.086) i g 35.9 n 107.2 (0.083) i	i 103.8 (0.092) n 27.8 g
5	18.0	65.4	5.82	1.12	18.90	g 50.2 s_A 57.9 (0.24) n 110.0 (0.055) i g 42.8 n 109.9 (0.056) i	i 106.2 (0.064) n 40.2 g
6	23.0	83.3	6.81	1.09	22.20	g 51.2 s_A 65.2 (0.30) n 110.9 (0.046) i g 45.3 n 110.2 (0.049) i	i 107.1 (0.058) n 42.4 g
7	26.0	69.7	8.13	1.08	26.50	g 48.1 s_A 67.3 (0.31) n 110.5 (0.043) i g 42.3 n 109.9 (0.055) i	i 105.7 (0.061) n 38.3 g
8	30.0	65.1	8.65	1.10	28.10	g 50.1 s_A 72.3 (0.37) n 111.5 (0.046) i g 43.3 n 111.4 (0.055) i	i 106.4 (0.055) n 41.3 g

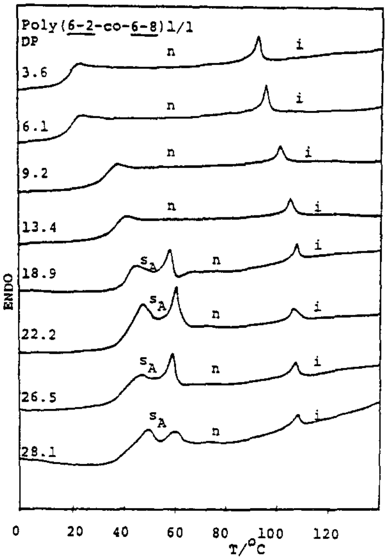

Figure 2a: First heating DSC scans of poly(6-2-co-6-8)1/1.

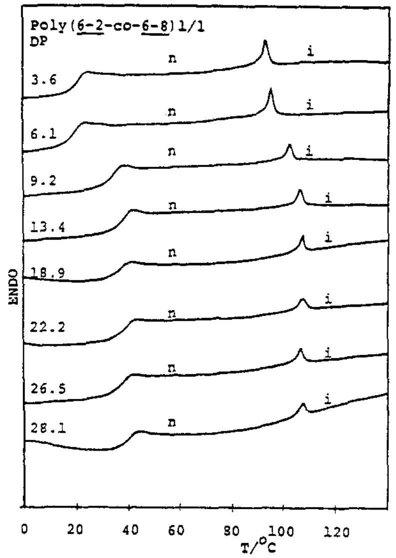

Figure 2b: Second heating DSC scans of poly(6-2-co-6-8)1/1.

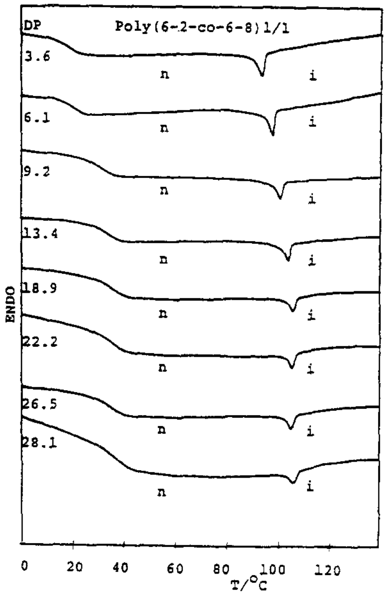

Figure 2c: Cooling DSC scans of poly(6-2-co-6-8)1/1.

Due to its close proximity to the copolymer glass transition temperature, the s_A phase does not appear in the second heating and cooling scans. This proximity transforms the s_A phase into a kinetically controlled mesophase.

Both thermal transition temperatures and their thermodynamic parameters are summarized in Table I. The thermal transition temperatures from the first and second heating scans are plotted in Figure 3a. The thermal transition data from the cooling scans are plotted in Figure 3b. These figures demonstrate that the phase behavior of poly(6-2-co-6-8)1/1 is, as expected, molecular weight dependent.

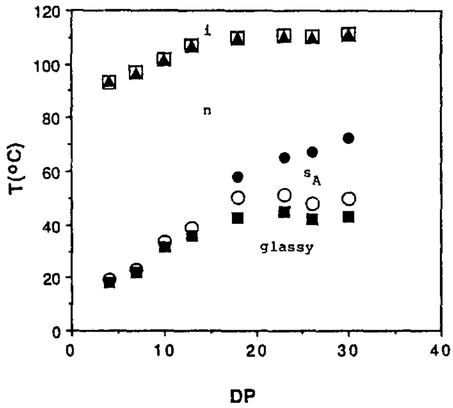

Figure 3a: Thermal transition temperatures of poly(6-2-co-6-8)1/1:
□ -Tn-i (first heating scan),
▲ -Tn-i (second heating scan),
● -Ts_A-n (first heating scan),
○ -Tg (first heating scan),
■ -Tg (second heating scan)

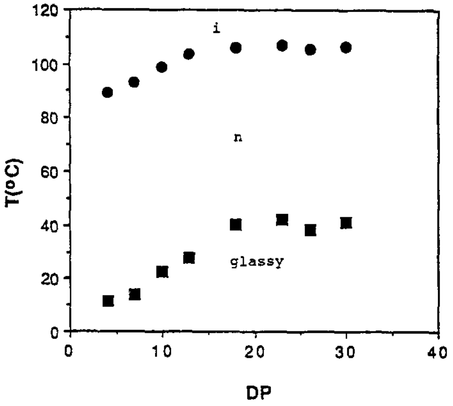

Figure 3b: Thermal transition temperatures of poly(6-2-co-6-8)1/1 obtained from the cooling scans: ● -Ti-n, ■ -Tg

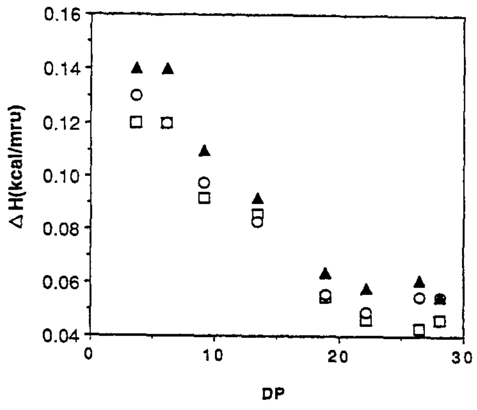

Figure 4: $\Delta H_{n\text{-}i}$ and $\Delta H_{i\text{-}n}$ of poly(6-2-co-6-8)1/1.
□ -ΔH (first heating scan),
○ -ΔH (second heating scan),
▲ -ΔH (cooling scan)

Finally, the enthalpy changes associated with the nematic-isotropic phase transitions collected from the first and second heating scans and the isotropic-nematic phase transitions collected from the cooling scans are plotted as a function of the degree of polymerization in Figure 4. This enthalpy change continuously decreases with the increase of the degree of polymerization. Presently, we do not have any good explanation for this trend.

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