Polymer Bulletin 25, 131–137 (1991)

Polymer Bulletin

Molecular engineering of liquid crystal polymers by living polymerization

7. Influence of copolymer composition on the phase behavior of poly{11-[(4-cyano-4′-biphenyl)oxy]undecanyl vinyl ether-co-2-[(4-cyano-4′-biphenyl)oxy]ethyl vinyl ether}

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SUMMARY

This paper describes the synthesis of poly{11-[4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether-co-2-[(4-cyano-4'-biphenyl)oxy]ethyl vinyl ether} A/B {poly[(6-11)-co-(6-2)]A/B} where A/B refers to the molar ratio between the monomers 6-11 and 6-2, with number average molecular weights above 15, by living cationic polymerization. The phase behavior of the resulting copolymers was discussed as a function of copolymer composition. Within this range of molecular weights, in the first heating scan poly(6-11) exhibits a melting and an enantiotropic s_A phase, while poly(6-2) an inverse s_C phase. In the second and subsequent heating scans poly(6-11) displays an enantiotropic s_X (unidentified smectic phase) and a s_A mesophase, while poly(6-2) only a glass transition temperature. Depending on composition, poly[(6-11-co-6-2)]A/B either display an enantiotropic nematic, enantiotropic s_A or both enantiotropic nematic and anantiotropic s_A phases.

INTRODUCTION

Previous papers from this series and from other laboratories demonstrated that group transfer polymerization of mesogenic methacrylates[1] and cationic polymerization of mesogenic vinyl ethers[2-7] can be performed under living polymerization conditions. For the cationic polymerization of vinyl ethers, Lenz's group uses the HI/I_2 initiating system which requires low polymerization temperatures and nonpolar solvents[8], while we use the initiating system $CF_3SO_3H/(CH_3)_2S$ which can induce living polymerization in polar solvents like CH_2Cl_2 and at 0°C.[9] The first series of experiments performed by both research groups are attempting to elucidate the dependence between the polymer molecular weight and phase behavior.[1-7] We also have reported the first series of quantitative experiments on the influence of copolymer composition on the phase behavior of a copolymer synthesized from two different mesogenic vinyl ethers.[5] The goal of this paper is to describe the influence of copolymer composition on the phase behavior of poly{11-[(4-cyano-4'-biphenyl)oxy}undecanyl vinyl ether-co-2-[(4-cyano-4'-biphenyl)oxy]ethyl vinyl ether} with molecular weights higher than the molecular weight below which phase transitions are molecular weight dependent.

EXPERIMENTAL

Scheme I outlines the synthesis of the poly[(6-11)-co-(6-2)]A/B.

Materials

2-[(4-Cyano-4'-biphenyl)oxy]ethyl vinyl ether (6-2)[5] and 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether (6-11)[2] of purities higher than 99.9% were synthesized as described previously. Methyl sulfide (anhydrous, 99%, Aldrich) was refluxed over 9-borabicyclo[3,3,1]nonane (crystalline, 98%, Aldrich) and then distilled under argon. Dichloromethane (99.6%, Aldrich) used as polymerization solvent

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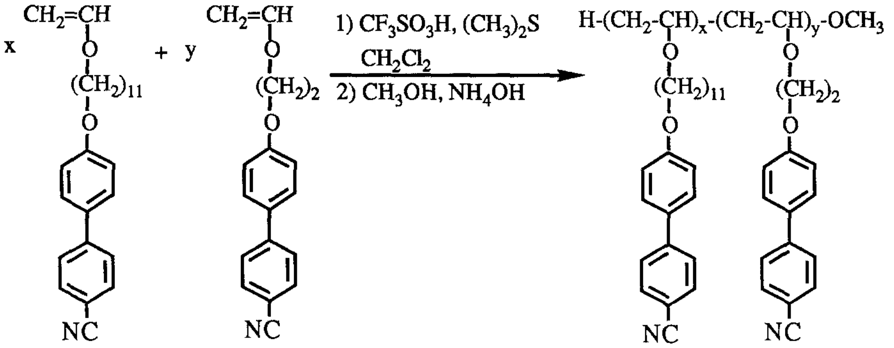
*To whom offprint requests should be sent was first washed with concentrated sulfuric acid, then with water, dried over magnesium sulfate, refluxed over calcium hydride and freshly distilled under argon before each use. Trifluoromethane sulfonic acid (triflic acid, 98%, Aldrich) was distilled under vacuum.



Scheme I
Synthesis of poly[(6-11)-co-(6-2)]A/B

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 or 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. First heating scans differ from second and subsequent heating scans. However, second and subsequent heating scans are identical. The first heating scans can be reobtained after proper annealing of the polymer sample. 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 texture. 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. High pressure chromatography experiments were performed with the same instrument.

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 methylene chloride, dimethyl sulfide and triflic acid were added via a syringe. The monomer concentration was about 10 wt% of 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 the $[M]_o/[I]_o$ ratio. At the end of the polymerization the reaction mixture was precipitated 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. Table I summarizes the polymerization results. Although the polymer yields are lower than expected due to losses during the purification process, the conversions were almost quantitative in all cases.

RESULTS AND DISCUSSION

The influence of molecular weight on the phase transitions of poly(6-11) was reported in a previous publication.[2] In the first heating scan poly(6-11) exhibits a melting transition followed by an enantiotropic s_A mesophase. In the second heating scan poly(6-11) with degrees of polymerization lower than 3 exhibit a melting and an enantiotropic s_A mesophase. Polymers with degrees of polymerization between 4 and 15 exhibit only the enantiotropic s_A mesophase, while those with degrees of polymerization higher than 20 an enantiotropic s_X (unidentified smectic phase) and an enantiotropic s_A mesophase. The phase transitions of poly(6-11) with degrees of polymerization higher than 15 are almost molecular weight independent. The influence of molecular weight on the phase behavior of poly(6-2) was investigated by Sagane and Lenz[7c] and reinvestigated by us.[9] Poly(6-2) with degrees of polymerization higher than 6 exhibit an inverse monotropic s_C phase only in the first heating scan.[7c,9] In the second heating scan they exhibit only a glass transition temperature. Therefore, in order to avoid the complication of the phase behavior due to the polymer molecular weight, we decided to investigate poly[(6-11)-co-(6-2)] with degrees of polymerization higher than 15. The synthesis of this copolymer is illustrated in Scheme 1. Table I summarizes the polymerization and copolymerization conditions, the molecular weights and the compositions of the resulting copolymers.

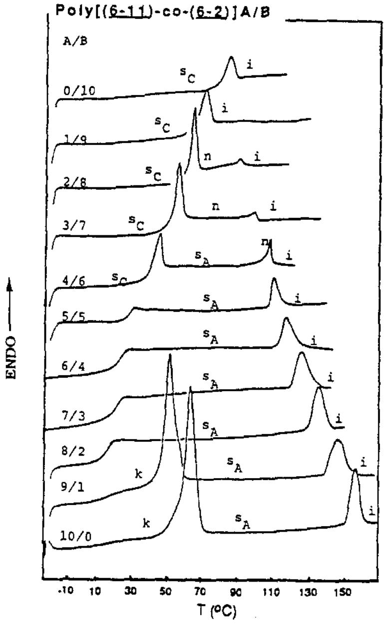


Figure 1a: First heating DSC scans of poly[(6-11)-co-(6-2)]A/B.

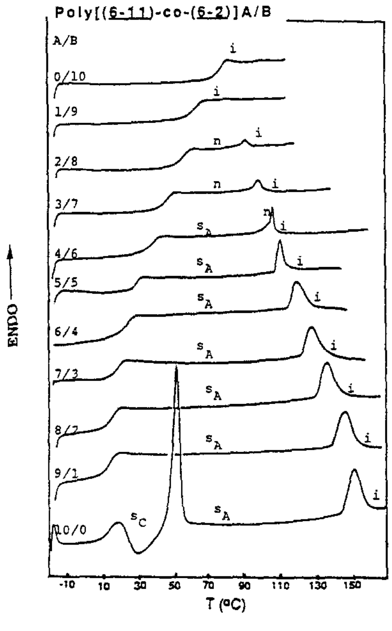


Figure 1b: Second heating DSC scans of poly[(6-11)-co-(6-2)]A/B.

Table I. Cationic Polymerization of 6-11 with 6-2 (polymerization temperature, 0°C; polymerization solvent, CH_2Cl_2; $[M]o=[6\text{-}11+6\text{-}2]=0.255\text{-}0.377M$; $[M]_o/[I]_o=20$; $[(CH_3)_2S]_o/[I]_o=10$; polymerization time, 1hr) and Characterization of the Resulting Copolymers.

Sample no.	[6-11]/[6-2] (mol/mol)	Polymer yield(%)	GPC			phase transitions (°C) and corresponding enthalpy changes (kcal/mru)	
			Mnx10^{-3}	Mw/Mn	DP	heating	cooling
1	0/10	64.8	4.56	1.18	17.2	s_C 85.7 (0.25) i g 78.3 i	i 70.5 g
2	1/9	72.4	4.12	1.26	15.0	s_C 70.5 (0.44) i g 64.8 i	i 56.6 g
3	2/8	73.9	4.18	1.09	15.0	s_C 64.4 (0.47) n 90.8 (0.038) i g 55.8 n 90.6 (0.044) i	i 86.7 (0.044) n 50.0 g
4	3/7	70.0	4.66	1.13	15.6	s_C 55.9 (0.55) n 98.5 (0.086) i g 44.1 n 98.5 (0.091) i	i 96.0 (0.085) n 41.6 g
5	4/6	71.4	4.74	1.12	15.0	s_C 42.8 (0.35) s_A 103.2 (-)* n 105.7 (0.18)*i g 35.8 s_A 103.0 n 105.6 (0.17)i	i 102.4 (-)* n 96.5 (0.18)* s_A 30.8 g
6	5/5	62.2	5.55	1.15	17.0	g 30.0 s_A 110.8 (0.34) i g 28.9 s_A 110.6 (0.34) i	i 109.2 (0.35) s_A 24.2 g
7	6/4	65.7	5.85	1.16	17.2	g 22.5 s_A 119.1 (0.45) i g 20.0 s_A 120.1 (0.47) i	i 116.6 (0.54) s_A 17.5 g
8	7/3	61.5	6.99	1.16	19.8	g 16.7 s_A 128.8 (0.58) i g 15.0 s_A 127.1 (0.62) i	i 124.6 (0.63) s_A 13.3 g
9	8/2	68.5	6.68	1.20	18.2	g 15.0 s_A 136.3(0.76) i g 14.8 s_A 135.8 (0.71) i	i 130.1 (0.79) s_A 8.4 g
10	9/1	53.9	8.90	1.12	22.9	g 16.7 k 52.1 (2.13) s_A 145.8 (0.81) i g 13.3 s_A 145.8 (0.80) i	i 138.9 (0.80) s_A 7.5 g
11	10/0	72.0	7.65	1.09	19.5	g 15.0 k 62.7 (2.82) s_A 153.3 (0.82) i g 12.5 s_X 50.4(1.74) s_A 151.7 (0.80) i	i 142.8 (0.82) s_A 19.8 (0.75) s_X 8.5 g

* overlapped peaks

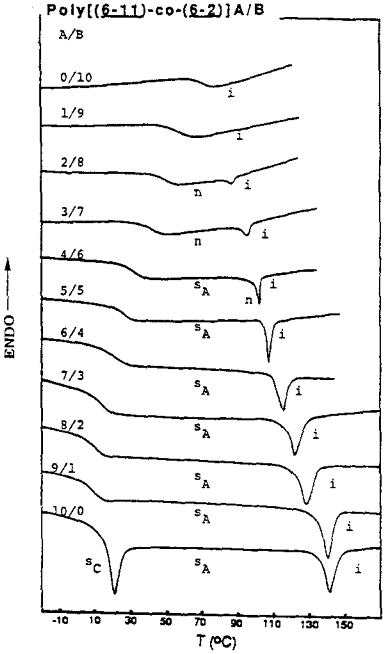


Figure 1c: Cooling DSC scans of poly[(6-11)-co-(6-2)]A/B.

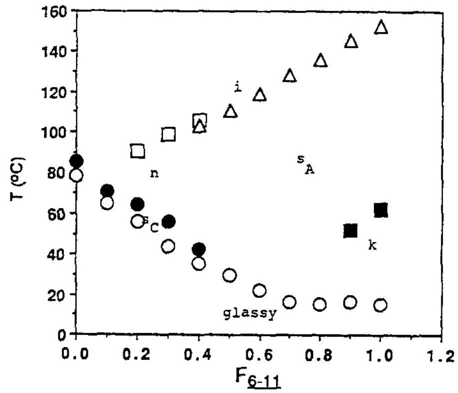


Figure 2a: Thermal transition temperatures of poly[(6-11)-co-(6-2)]A/B. Data from first DSC heating scans.

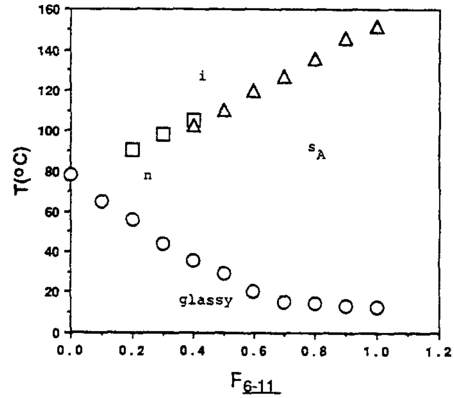


Figure 2b: Thermal transition temperatures of poly[(6-11)-co-(6-2)]A/B. Data from second DSC heating scans.

Figure 1a, b, c present the first and second heating and respectively the first cooling DSC scans of poly[(6-11)-co-(6-2)]A/B where A/B refers to the mole ratio between the 6-11 and 6-2 monomeric structural units in copolymer. In the first heating scan poly(6-2) and poly[(6-11)-co-(6-2)]1/9 display an inverse monotropic s_C mesophase (Figures 1a,c). Poly[(6-11)-co-(6-2)] with A/B=2/8 and 3/7 exhibit in the first heating scan an inverse monotropic s_C phase and an enantiotropic nematic phase. In the second heating scan these copolymers exhibit only the enantiotropic nematic mesophase. Poly[(6-11)-co-(6-2)]4/6 presents the most interesting behavior. In the first heating scan it displays the inverse monotropic s_C and enantiotropic s_A and nematic mesophases, while in the second heating scan only the last two phases. Regardless of the DSC heating scan, poly[(6-11)-co-(6-2)] with A/B=5/5 to 8/2 exhibit an enantiotropic s_A mesophase. Poly[(6-11)-co-(6-2)]9/1 displays a crystalline melting only in the first heating scan and an enantiotropic s_A phase in all other DSC scans, while poly(6-11) behaves as described in the previous publication[2] and briefly recapitulated at the begining of this paper.

The thermal transition temperatures and their corresponding thermodynamic parameters are summarized in Table I. The thermal transition temperatures collected from the first heating scan are plotted in Figure 2a, those from second heating scan in Figure 2c. Glass transition temperatures are also plotted in these figures. The enthalpy changes associated with these transitions are plotted in Figure 3.

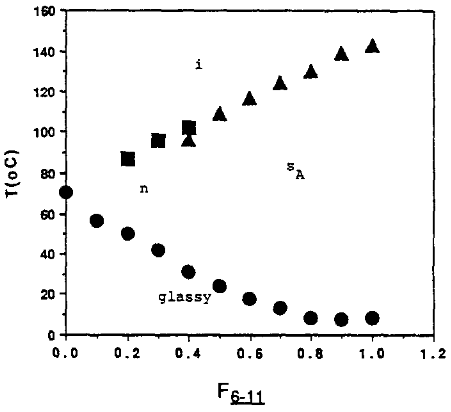


Figure 2c: Thermal transition temperatures of poly[(6-11)-co-(6-2)]A/B. Data from cooling DSC scans.

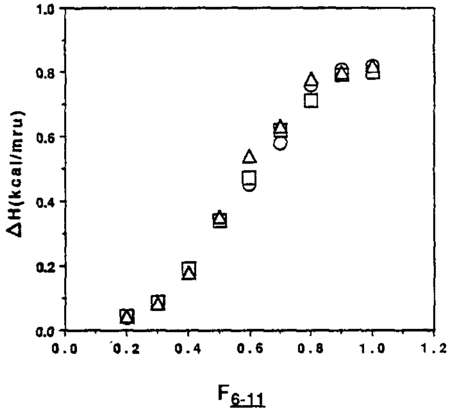


Figure 3: ΔH of isotropization of poly[(6-11)-co-(6-2)]A/B copolymers
○ -ΔH (first heating scan),
□ -ΔH (second heating scan),
△ -ΔH (cooling scan).

The phase behavior of poly[(6-11)-co-(6-2)]A/B demonstrates the capability to molecular engineer the phase behavior of side chain liquid crystalline polymers by copolymerization. The most interesting result refers to the ability to tailer make noncrystallizable copolymers exhibiting either enantiotropic nematic or s_A mesophases or both enantiotropic s_A and nematic mesophases.

ACKNOWLEDGMENTS

Financial support of this research by the Office of Naval Research is gratefully acknowledged.

REFERENCES

1. V. Percec, D. Tomazos and C. Pugh, *Macromolecules*, 22, 3259(1989)
2. V. Percec, M. Lee and H. Jonsson, *J. Polym. Sci. Polym., Chem. Ed.*, in press
3. V. Percec and M. Lee, *Macromolecules*, in press
4. V. Percec, H. Jonsson and A. Hult, *Polym. Bull.*, in press
5. V. Percec and M. Lee, *Polymer*, in press

6. V. Percec and M. Lee, *Polym. bull.*, submitted
7. T. Sagane and R. W. Lenz, (a) *Polym. J.*, **20**, 923(1988); (b) *Polymer*, **30**, 2269(1988); (c) *Macromolecules*, **22**, 3763(1989)
8. T. Higashimura and M. Sawamoto, in "*Comprehensive Polymer Science*", vol. 3, Allen G. and J. Bevington Eds., Pergamon Press, Oxford, 1989, p. 684
9. V. Percec and M. Lee, to be published

Accepted September 25, 1990 K