# Macromolecules

Volume 25, Number 5 March 2, 1992

## Synthesis and Characterization of Rigid-Rod Star-Block Copolymers of a Varying Number of Arms

**S. K. Bhattacharya,* C. A. Smith, and W. H. Dickstein**[†]

*IBM Research Division, Almaden Research Center, 650 Harry Road,*
*San Jose, California 95120-6099*

*Received February 25, 1991; Revised Manuscript Received September 30, 1991*

ABSTRACT: The synthesis and initial characterization of rigid-rod star-block copolymers exhibiting thermotropic mesophases are described. The copolymers consisted of flexible poly(dimethylsiloxane) cores having two to six arms, at the ends of which 4-[(methoxybenzoyl)oxy]benzoic acid mesogens were attached through amide linkages. The siloxane arm lengths were kept constant at approximately 2500 $M_n$. These block copolymers were of very well-defined structures with narrow molecular weight distributions. They were characterized by thermal and optical techniques. Clear evidence of phase separation between the flexible segments and the rigid blocks was obtained by the invariance of the low-temperature glass transition phenomena observed corresponding to the glass transition of the siloxane homopolymer. All the polymers of this series showed nematic liquid-crystalline texture in optical microscopy.

### Introduction

Liquid-crystalline (LC) polymers exhibit the unique property of self-organization to ordered structures in the liquid state and maintain the order in the subsequent solid state. Extensive research work is being carried out in the field of liquid-crystalline polymers in order to exploit these properties,[1-4] and many polymers with variations in the structure of the classical LC polymer have been synthesized, e.g., structures with mesogens in the main chain or in the side chain or both, structures with or without flexible spacers in the main or side chain, and structures containing asymmetric substitutions leading to frustrated chain packing, to name a few.[5-8] LC polymers, however, suffer from the distinct disadvantage of having poor properties in the direction perpendicular to the direction of their chain extension. In fact, it has been theoretically shown that for LC polymers the modulus perpendicular to the draw direction is proportional to the cohesive energy density of the polymer.[9] Different solutions to this problem have been proposed. Takayanagi and co-workers have suggested the use of LC block copolymers consisting of flexible blocks, the latter acting as tie chains between the LC domains and thus improving strength in the transverse direction.[10] Some other suggestions involve the introduction of biaxiality in the LC state either externally or by chemical means.[3,11] Recently the idea of using thermotropic rigid-rod star block copolymers for this purpose has been suggested in the literature,[12,13] the rationale being the same as using LC block copolymers having flexible blocks. A higher degree of entanglement has been additionally introduced by increasing the number of arms to more than two. The two-arm rigid star-block copolymer essentially has a triblock structure. This paper reports the synthesis of star-block thermotropic LC copolymers consisting of one to four and six arms, respectively. These copolymers consist of a poly(dimethylsiloxane) star core at the end of which amide/ester mesogenic units are attached. Figure 1 shows the sketch of a typical four-arm copolymer. Thermal characterization of these polymers by DSC and TGA and optical characterization by hot-stage optical microscopy is also reported.

### Experimental Section

**Materials**: Poly(dimethylsiloxane) was prepared via the utilization of the blocked amine functional anionic initiator *p*-[*N*,*N*-bis(trimethylsilyl)amino]styrene, which is soluble in nonpolar solvents. The multiarm structures were achieved by using multifunctional terminating agents. Chlorotrimethylsilane, dichlorodimethylsilane, trichloromethylsilane, tetrachlorosilane, and 1,2-bis(trichlorosilyl)ethane were used as terminating agents for making one- to four-arm and six-arm star polymers, respectively. The detailed procedure of the synthesis is given in the literature.[14,15] 1,2-Bis(trichlorosilyl)ethane was obtained from Petrarch Systems, and all other silanes were obtained from Aldrich; all the silanes were titrated prior to use.[12] *sec*-Butyllithium in hexane was also obtained from Aldrich and titrated before use. Hexane, hexamethylphosphoramide (HMPA), and benzene were obtained and purified as described in ref 12. The pertinent properties of the telechelic poly(dimethylsiloxane) intermediates are shown in Table I.

---

* All correspondence should be addressed to this author at Hindustan Lever Limited, Research Centre, I. C. T. Link Road, Chakala, Andheri (East), Bombay—400099, India.

[†] Deceased.

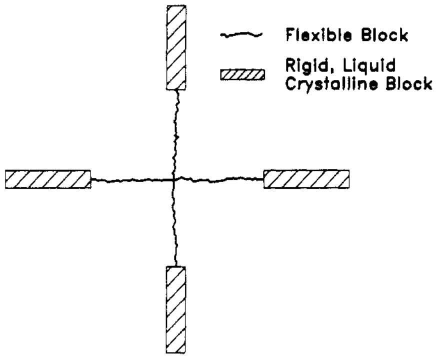

**Figure 1.** Schematic diagram of a four-arm rigid-rod star-block copolymer.

**Table I**
**Summary of Telechelic Siloxanes**

| polymer | no. of arms | $M_n$(theory)[a] | $M_n$(found)[b] | $M_w/M_n$[c] |
|---|---|---|---|---|
| ST-I | 1 | 2500 | 2750 | 1.10 |
| ST-II | 2 | 2500 | 3250 | 1.14 |
| ST-III | 3 | 2500 | 3200 | 1.18 |
| ST-IV | 4 | 2500 | 4100 | 1.20 |
| ST-V | 6 | 2500 | 2850 | 1.23 |

[a] Theoretical $M_n$ based on [(monomer)/(initiator)] × (monomer $M_w$). [b] $M_n$ calculated by end-group analysis from $^1$H NMR results. [c] $M_w/M_n$ based on polystyrene-calibrated GPC in THF with no correction for broadening.

**Preparation of thermotropic rigid-rod star-block copolymers**: The synthesis of six-arm thermotropic star-block copolymer is described as follows; the copolymers with other number of arms were also prepared in the same manner. In a clean, dry, argon-filled 250-mL round-bottomed flask, equipped with a magnetic stirrer, was placed 0.0172 mol of 4-[(4-methoxybenzoyl)oxy]benzoyl chloride, and 20 mL of pyridine was added. Then the solution was heated to 65 °C in an oil bath, and to it was added a 24.5-mL benzene solution containing 4 g of the six-arm telechelic poly(dimethylsiloxane) intermediate (ST-V in Table I). The reaction was allowed to proceed for 48 h, and after that 20 mL of distilled water was added. The precipitate was collected by vacuum filtration; the product was taken up in 100 mL of boiling tetrahydrofuran and filtered to remove the unreacted 4-[(4-methoxybenzoyl)oxy]benzoic acid. The filtrate was condensed in a rotary evaporator. The resulting material was dissolved in a minimum amount of THF and precipitated in a 1:1 (v/v) mixture of methanol and water to give a slightly yellowish rubbery solid (yield 90%). The copolymers containing different numbers of arms were almost of the same physical appearance. All polymers were characterized by qualitative infrared spectroscopy, gel permeation chromatography, differential scanning calorimetry, thermogravimetric analysis, and optical microscopy.

**Measurements**: Qualitative IR spectroscopy was performed in chloroform using an IBM IR-32 spectrometer to detect the amidation of the amine telechelic poly(dimethylsiloxane)s. The actual number-average molecular weight per arm of the telechelic poly(dimethylsiloxane)s was determined by NMR spectroscopy from end-group analysis, using an IBM Instruments AF 250 NMR operating at 250 MHz. GPC of the telechelic intermediates and the final copolymers was performed with a Waters 150-C chromatograph. DSC was done using a Du Pont 910 DSC, and a Perkin-Elmer TGS-2 was used for thermogravimetric analysis. An Axiomat optical microscope by Zeiss was used for microscopy in conjunction with a Mettler hot stage.

## Results and Discussion

The copolymer with one arm, in other words the diblock copolymer, was a waxy solid, white in color. All other copolymers were rubbery solids of slightly yellow color. GPC results showed that the narrow molecular weight distribution of the telechelic siloxanes was maintained in the final copolymers.

**Table II**
**TGA[a] Results of the Copolymers**

| polymer | temp of 5% wt loss, °C | max degradation temp, °C |
|---|---|---|
| ST-T-I | 314 | 493 |
| ST-T-II | 328 | 469 |
| ST-T-III | 339 | 476 |
| ST-T-IV | 353 | 473 |
| ST-T-V | 332 | 466 |

[a] TGA was done under a $N_2$ atmosphere at the rate of 10 °C/min.

**Table III**
**Transition Temperatures and the Corresponding Enthalpies of the Siloxane Segments of the Thermotropic Block Copolymers**

| polymer | $M_n$/arm[a] | $M_n$[b] | $T_g$, °C | $T_m$, °C | $\Delta H$ heat of melting, J/g |
|---|---|---|---|---|---|
| ST-T-I | 2750 | 3050 | −113 | −43 | 23.8 |
| ST-T-II | 3250 | 8750 | −114 | −49 | 16.9 |
| ST-T-III | 3200 | 9500 | −106 | −59 | 8.0 |
| ST-T-IV | 4100 | 9150 | −117 | −56 | 13.8 |
| ST-T-V | 2850 | 14000 | −107 | −60 | 1.5 |

[a] $M_n$ calculated by end-group analysis from $^1$H NMR results. [b] $M_n$ of copolymers determined from GPC in THF based on polystyrene standards with no correction for broadening.

The thermal stabilities of the copolymers are shown in Table II. All the copolymers showed good thermal stability under an inert nitrogen atmosphere. The temperature of 5% weight loss was found to increase while the temperature of maximum degradation was found to decrease with the increase in the number of arms of the copolymers. No particular reason could be given at the present moment.

Table III shows the thermal analysis results obtained by low-temperature DSC experiments. In all the copolymers a low-termperature glass transition was observed corresponding to the glass transition of poly(dimethylsiloxane) homopolymer. This is clear evidence of a phase separation between the siloxane segments and the rigid mesogens. Taking into consideration the variation in the molecular weight between the copolymers, it appears that the glass transition temperatures of the siloxanes increase with an increase in the number of arms. This could be explained by the fact that a higher number of arms leads to higher entanglements resulting in a higher threshold of energy needed for the onset of segmental motion in the flexible units. The higher heat of melting of ST-T-IV is probably because of its higher arm length, which helps the terminal mesogens arrange in a more orderly fashion. The copolymers showed cold crystallization and subsequent melting of the siloxane segment of the copolymers, the heat of melting and the melting temperature decreasing with an increase in the number of arms. Earlier experiments have shown that the star nature of the siloxane blocks inhibits crystallization of the siloxane blocks.[13] For the same reason, as the number of arms increases, the inhibition to crystallization increases and this is apparent from the enthalpy of melting results.

Typical thermograms for the three-arm copolymer in the first and second heating cycles are shown in Figure 2. It was attempted to determine the glass transition and the melting temperatures of the mesogenic units by DSC. This was, however, not very successful because the thermograms in both the first and second heating cycles were not smooth and showed multiple transitions, not allowing definitive conclusions to be drawn from the thermograms.

In hot-stage microscopy with the one-arm copolymer schlieren texture accompanied with large-scale flow was observed at 85 °C. The nematic schlieren texture was confirmed by the presence of singularities with two as

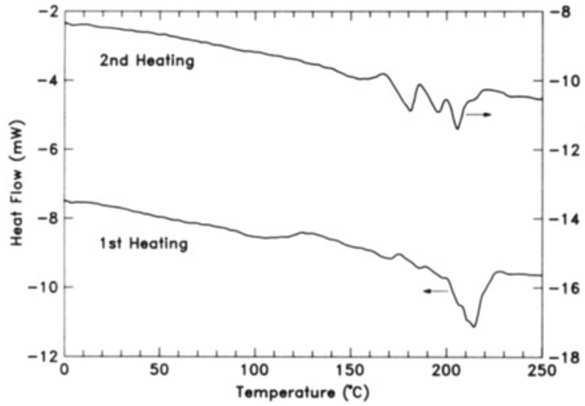

**Figure 2.** DSC thermograms of ST-T-III in the first and second heating cycles.

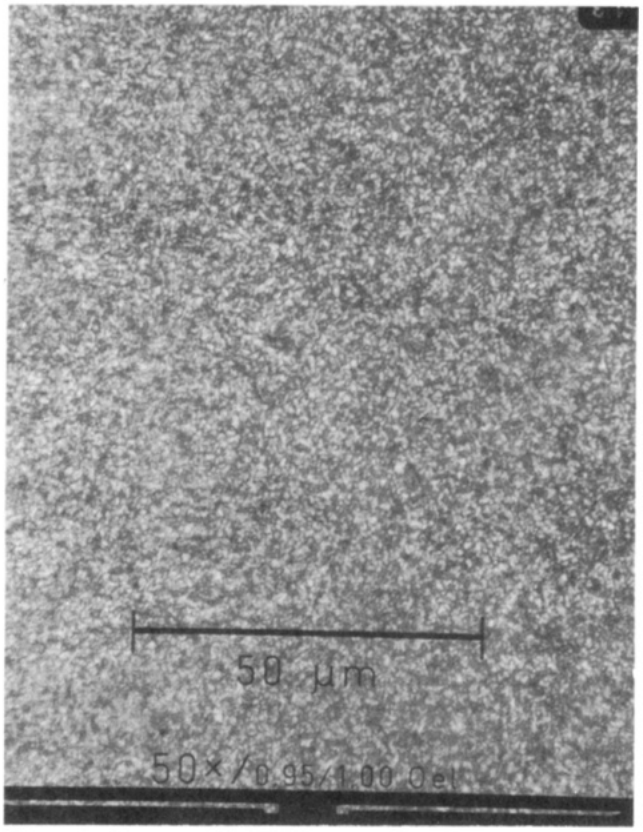

**Figure 3.** Texture of ST-T-III at 150 °C, under cross polarizers.

well as four associated brushes ($S = \pm 1/2$ and $\pm 1$). The two-arm copolymer started deforming from 97 °C under shear. It was found to melt at 112 °C to give schlieren texture, and large-scale flow set in at 150 °C. The three-arm polymer started melting from 121 °C, melting was complete by 145 °C, and the polymer exhibited significant flow above 168 °C. The first broad low-temperature endotherm (80–120 °C) in the first heating cycle in Figure 2 possibly indicates softening of the polymer, and the second broad low-temperature endotherm (120–170 °C) possibly indicates melting. No definitive optical events other than large-scale flow could be detected corresponding to the large endotherm at 214 °C with multiple shoulders. In the case of the four-arm copolymer, softening was observed at 96 °C, melting at 100 °C, and large scale flow at 160 °C. For the six-arm copolymer, softening at 100 °C and melting at 120 °C were observed. No isotropization was observed in any of these polymers up to 250 °C. All of these polymers showed schlieren texture upon melting up to the maximum temperature of the study, 250 °C. Figure 3 shows a typical texture for the three-arm copolymer in the mesophase. All these polymers exhibited two-phase texture on being cooled slowly from the anisotropic melt to 25 °C. Figure 4 shows a typical texture of the four-arm polymer on being cooled to room temperature from 200 °C at the rate of 10 °C/min. Not much difference was observed in the texture of the copolymers with different numbers of arms in the liquid-crystalline state as well in the solid state upon being cooled from the liquid-crystalline state.

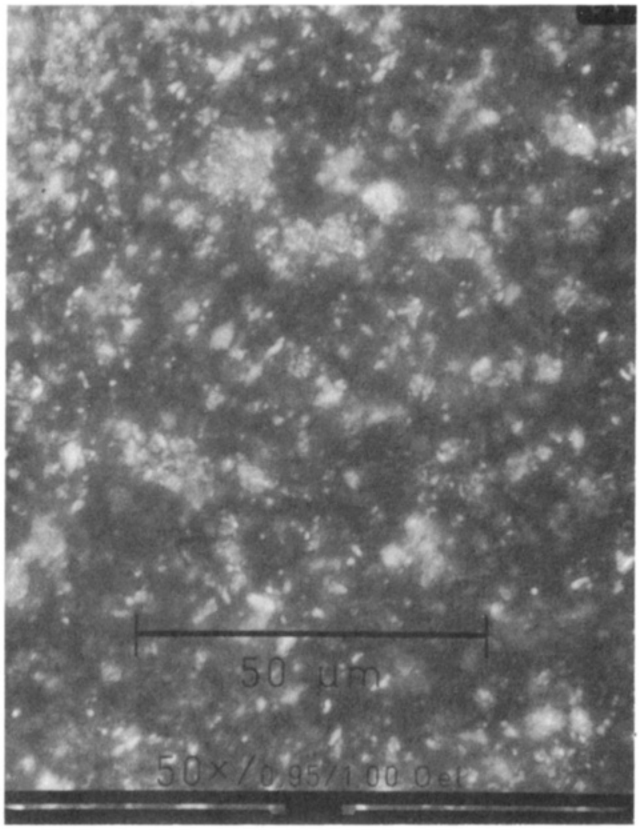

**Figure 4.** Texture of ST-T-IV at room temperature, having been cooled from 200 °C, under cross polarizers.

Thus two-phase morphology was observed in the solid state for rigid-rod star-block copolymers having different numbers of arms. In a previous paper it was reported that this type of polymer shows phase separation in the solid state depending on the length of flexible units.[13] It was also reported that a longer siloxane segment essentially decouples the motion of the mesogens from that of the core. In the present work, the arm length was chosen in such a way that the resulting copolymers do show phase separation. However, changes in arm number showed no effect on phase separation in the samples under investigation. Further work is in progress in order to ascertain the effect of an increase in the number of arms in these copolymers on the flow behavior. Because of the interesting architecture of these molecules, detailed characterization of these materials could result in an increased understanding of the role of molecular architecture on the morphology of polymeric systems.

## References and Notes

(1) Jackson, W. J., Jr. *Br. Polym. J.* **1980**, *12*, 150.
(2) Antoun, S.; Lenz, R. W.; Jin, J. I. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1901.
(3) Krigbaum, W. R.; Ciferri, A.; Asrar, I. *Mol. Cryst. Liq. Cryst.* **1981**, *76*, 79.
(4) Calundun, G. W. (Celanese Corp.). U.S. Patent 4,161,670, 1979.

(5) Roviello, A.; Sirigu, A. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 455.
(6) Jin, J. I.; Antoun, S.; Ober, C.; Lenz, R. W. *Liq. Cryst. Polym. Symp.* **1980**.
(7) Shibaev, V. P.; Moisseenki, V. M.; Faiedzoa, T. S.; Plate, N. A. *Eur. Polym. J.* **1980**, *16*, 277.
(8) Reck, B.; Ringsdorf, H. *Makromol. Chem., Rapid. Commun.* **1985**, *7*, 389.
(9) Halliday, L.; White, J. W. *Pure. Appl. Chem.* **1971**, *26*, 545.
(10) Takayanagi, M.; Ogata, T.; Morikaws, M.; Kai, T. *J. Macromol. Sci., Phys.* **1980**, *817* (6), 591.
(11) Flood, J. E.; White, J. L.; Fellers, J. F. *J. Appl. Polym. Sci.* **1982**, *27*, 2965.
(12) Dickstein, W. H. Ph.D. Thesis, University of Massachusetts, 1987.
(13) Dickstein, W. H.; Lilliya, C. P. *Thermotropic Rigid Rod Star Block Copolymers*, in press.
(14) Dickstein, W. H.; Lilliya, C. P. *Macromolecules* **1989**, *22*, 3882.
(15) Dickstein, W. H.; Lilliya, C. P. *Macromolecules* **1989**, *22*, 3886.

**Registry No.** $MeOC_6H_4$-*p*-$CO_2C_6H_4$-*p*-COCl, 52899-54-4.