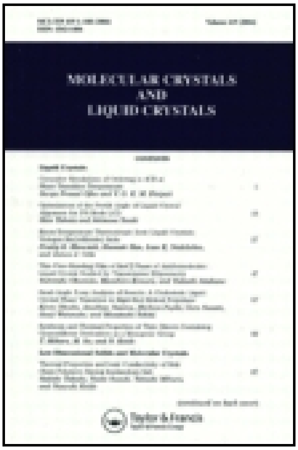

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Thermotropic Rigid rod Star-Block Copolymers

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THERMOTROPIC RIGID ROD STAR-BLOCK COPOLYMERS

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Abstract The synthesis and initial characterization of thermotropic star-block copolymers is described. Preparation of the copolymers involves affixing low molecular weight, acid functional thermotropic mesogens to the ends of unique amine telechelic star poly(dimethylsiloxane)s. The copolymers all contain the same mesogen, approximated by the model nematic compound 4-(4'-methoxybenzoyloxy)-4- n-butylbenzamide. The siloxane arm lengths were varied from approximately 600 to 6000 Mn. These block copolymers are very well-defined, with narrow molecular weight distributions and extents of mesogen attachment to the star core of greater than 95%. DSC clearly shows that the mesogenic blocks are phase separated from the nonpolar star cores. These waxy to rubbery solids melt to form initially homeotropic phases regardless of siloxane arm length, however, the star copolymer of shortest arm length does eventually form a highly birefringent, nonhomeotropic phase at higher temperatures.

INTRODUCTION

The field of thermotropic liquid crystalline polymers has progressed primarily along the paths of main chain[1,2] and side chain polymers[3,4]. These polymers have generally been prepared by reacting low molecular weight, end-functional thermotropic mesogens with end-reactive flexible spacers to result in the appropriate topology. A number of variables have been exercised in these studies including type and length of the flexible spacer, axial ratio and regularity of the mesogen, as well as the type of backbone used for side chain polymers.

More recent work has reported the preparation of thermotropic liquid crystalline polymers with mesogenic units in both the side and main chains[5]. Other work has reported the termination of oligimeric end-functional polyglycols with aromatic diester and diacid mesogenic units[6]. Both of these works have resulted in novel liquid crystalline polymers.

This paper will report the synthesis of the first star-block thermotropic liquid crystalline copolymers. These star-block copolymers, see Figure I, are comprised of a four-arm poly(dimethylsiloxane) star core at the extremities of which are attached amide/ester mesogenic units. Although only four-armed stars have been prepared up to this report, the synthesis of the siloxane star cores has been shown to be of sufficient generality such that the arm number could be readily varied up to eighteen using known methods[7]. In addition to the synthesis of these novel liquid crystalline copolymers, characterization performed to date will be reported.

EXPERIMENTAL

Materials: The telechelic poly(dimethylsiloxane) intermediates were prepared as described elsewhere and their pertinent properties are shown in Table I. p-Hydroxybenzoic acid, p-anisoyl chloride, 4-butylaniline, thionyl chloride, benzene, and pyridine were purified and dried by the usual manner. Chloroform (spectroscopic grade) was received from Fischer Scientific and used as received.

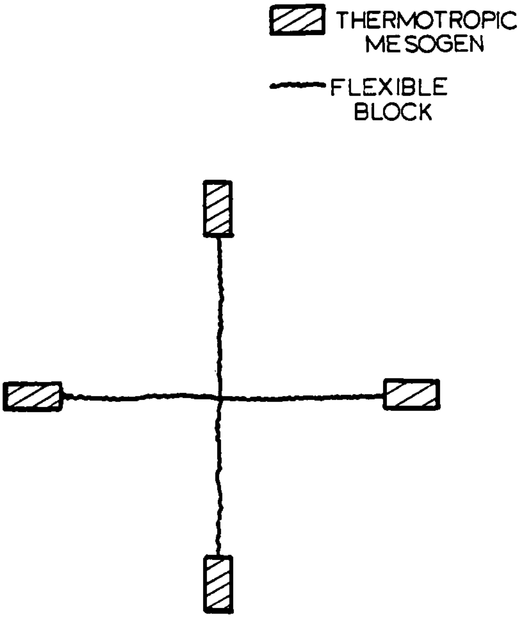

FIGURE 1. Representation of a thermotropic rigid rod star-block copolymer.

Preparation of 4-(4'-methoxybenzoyloxy) benzoic acid: This thermotropic liquid crystal was prepared similarly to previous accounts[8]. Upon melting at 221°C, this compound entered a nematic liquid crystalline phase which continued up to decomposition.

Preparation of 4-(4'-methoxybenzoyloxy)-4-n-butylbenzamide: This compound was prepared from the acid chloride of 4-(4'-methoxybenzoyloxy) benzoic acid and an excess of 4-butylaniline as described elsewhere[7]. The compound melted at 213°C into a nematic phase which persisted until the onset of degradation.

TABLE I. Summary of telechelic siloxanes.

Polymer	Mn (theo)*	Mn (found)#	Functionality+	Mw/Mn>
L-I	1500	1600 ± 200	1.9 ± 0.3	1.32
ST-I	3200	2600 ± 200	4.1 ± 0.3	1.32
ST-II	5100	3900 ± 500	3.7 ± 0.4	1.20
ST-III	9000	6190 ± 1100	3.7 ± 0.5	1.31
ST-IV	16,000	17,000 ± 2000	4.1 ± 0.4	1.32
ST-V	24,000	24,000 ± 2000	4.3 ± 0.5	1.27

* Theoretical Mn based on [(Monomer/(Initiator)]x(Monomer MW).

#Mn found via vapor phase osmommetry, chloroform @ 37°C. Polymers ST-IV and ST-V Mn based on GPC extrapolation.

+Functionality found via infrared spectroscopy of 1600 cm^{-1} phenyl ring vibration combined with Mn data.

>Mw/Mn based on polystyrene calibrated GPC in THF with no correction for broadening.

Preparation of a four-arm star thermotropic rigid rod star-block copolymer: Into an argon filled, clean, dry 25 mL round bottom flask containing 0.0184 moles of 4-(4'-methoxybenzoyloxy) benzoyl chloride was added 20 mL of pyridine. After heating to 65°C in an oil bath, 14 mL of a benzene solution containing 2.92 grams of ST-V (see Table I) telechelic poly(dimethylsiloxane) was added with vigorous stirring. The reaction proceeded under argon for 45 hours at 65°C at which time 10 mL of distilled water was added to insure total precipitation of the copolymer product. The precipitate was collected by filtration, the product was taken up in 100 mL of boiling tetrahydrofuran, filtered to remove the excess acid, and then condensed by removing the solvent via rotary evaporation. The resulting material was then dissolved into THF and reprecipitated into methanol several times to yield 2.92 grams (93% yield) of a rubbery solid. The copolymer was then characterized by qualitative and quantitative infrared spectroscopy, gel permeation chromatography, differential scanning calorimetry, thermal gravimetry, and optical microscopy.

This copolymer was found to melt at 201°C into a birefringent phase which persisted to at least 300°C, above which optical microscopy was not performed.

Measurements: Quantitative infrared spectroscopy was performed in chloroform and measured the extent of amidation of the amine telechelic poly(dimethylsiloxane)s based on a Beer's law plot of the model compound p-N-butylphyl-4'-anisamide.

Gel permeation chromatography was performed on a Waters chromatograph and optical microscopy was performed by placing a sample mounted between glass cover slips onto a hot stage between crossed polarizers. DSC and TGA were performed on Perkin-Elmer equipment.

RESULTS AND DISCUSSION

Figure 2 shows how the amine telechelic poly(dimethylsiloxane)s were converted into the thermotropic rigid rod star-block copolymers. This amidation reaction proceeded to at least 95% completion for the preparation of the one linear and five star-block copolymers described in this work. The copolymers formed were all solid materials and gel permeation chromatography showed that the narrow molecular weight distribution characteristic of the telechelic siloxanes was maintained in the final copolymers.

As expected, all of the copolymers showed clear evidence for phase separation of the siloxane segments from the rigid units. Low temperature DSC showed a low temperature glass transition temperature typical for dimethylsiloxane polymers for all of the copolymers near -120°C, and as shown in Table II, the linear copolymer and star-block copolymers of sufficiently long spacer length showed cold crystallization and melting of the siloxane segment of the copolymers. Clearly, under the conditions of the DSC experiment, the star nature of the copolymers inhibited crystallization of the siloxane blocks, especially at short siloxane block lengths.

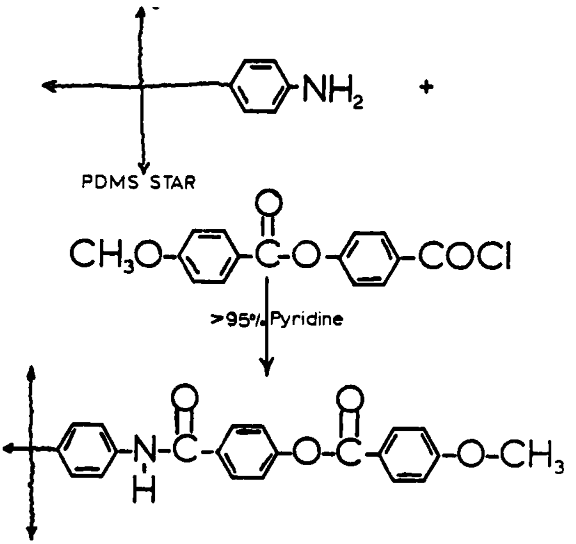

FIGURE 2. Synthesis of thermotropic rigid rod star-block copolymers.

The liquid crystallinity of the copolymers was explored by DSC and optical microscopy. Prior to preparing the copolymers, a suitable model compound for the rigid segment had to be prepared so that the final copolymer would qualify as a thermotropic rigid rod star-block copolymer. The model compound, 4-(4'-methoxybenzoyloxy)-4-n-butylbenzamide, was prepared to duplicate the ester/amide rigid unit that would be at the extremities of the copolymer chains. The model ester/amide was shown by optical mixing studies to go into a nematic liquid crystalline phase upon melting at 213°C.

TABLE II. Melting temperatures and enthalpies of melting of the siloxane segment of the thermotropic block copolymers.

Polymer	Mn/arm	Tmax (°C)*	Enthalpy (cal/g)
L-T-I	800	-39.5	0.55
ST-T-I	650	none	----
ST-T-II	975	none	----
ST-T-III	1550	-47.1	3.53
ST-T-IV	4250	-42.1	3.93
ST-T-V	6000	-37.9	5.14
ST-I#	650	none	----
ST-IV#	4250	-38.3	6.67

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* All runs performed on a Perkin-Elmer DSC-II at a heating rate of 20°C/min on samples quenched to -150°C from 50°C at a cooling rate of 320°C/min. Tmax is the maximum temperature of the peak of the melting endotherm.

These polymers are telechelic amine siloxanes; they are not thermotropic copolymers.

Table III gives the results of high temperature DSC analysis of the copolymers prepared in this work. A transition closely resembling a glass transition was apparent in all six of the copolymers prior to their melting endotherms. DSC experiments indicated that this apparent glass transition persisted on successive heatings, as well as on successive heatings that followed quick coolings from the melt. However, there remains some question as to whether this change in slope is truly a glass transition. This transition clearly requires further work for better understanding.

TABLE III. Glass transition temperatures, maximum melting temperatures, and enthalpy of melting transitions of rigid segment of copolymers.

Polymers	Mn/arm	%Cryst*	Tg	Tmax	Enthalpy<
L-T-I	800	33	77.5	143.5	1.00
ST-T-I	650	38	68.3	123.9	0.52
ST-T-II	975	29	54.1	166.7>	0.85>
ST-T-III	1550	21	91.0>	178.6>	0.23>
ST-T-IV	4250	9	88.9>	200.0>	0.05>
ST-T-V	6000	6	82.0>	201.0>	0.06>

#Measurements made at a heating rate of 10°C/min after a first heating to 210°C at 20°C/min followed by a 20°C/min cooling to 50°C.

* This value represents the fraction by weight of rigid, crystallizable segment in the copolymers

< All enthalpy of melting values in cal/gram

> These values are reported for a first heating at 20 °C/min.

Figure 3 shows a graph of the temperature of the maximum of the melting endotherm versus the poly(dimethylsiloxane) arm length for the melting of the rigid unit of the star-block copolymers. Clearly, as the arm length of the siloxane increases, the melting temperature of the mesogenic unit asymptotically approaches that of the ester/amide model compound. As does the data on the melting of the siloxane units of the star-block copolymers, this data also indicates a high degree of phase separation. The data also suggests a greater degree of perfection of the crystalline phase of the mesogenic unit with increasing arm length of the flexible siloxane.

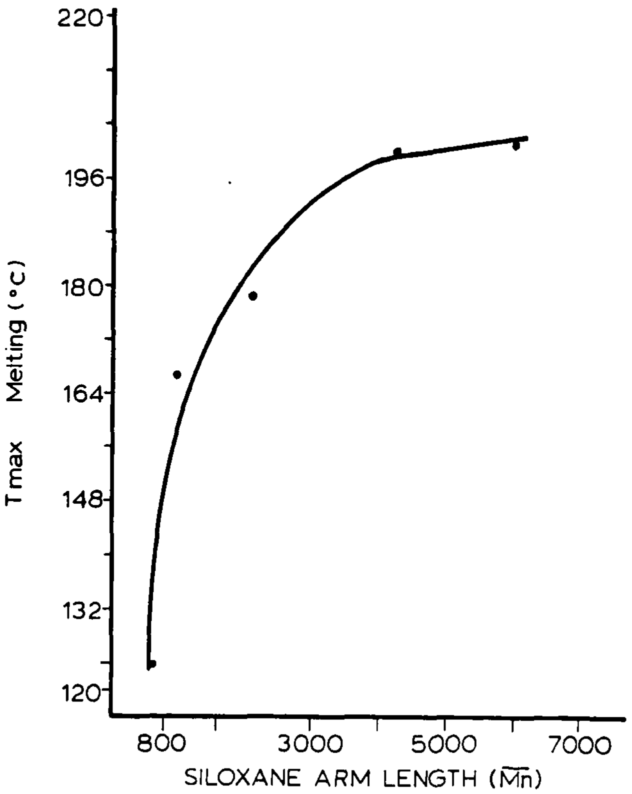

FIGURE 3. Tmax versus siloxane arm length.

Hot stage optical microscopy between crossed polarizers clearly showed that all six of the copolymers showed a liquid crystalline phase above their respective melting temperatures. All of the copolymers showed an initial homeotropic phase, which in the case of the linear and lowest molecular weight star-block copolymers, gave way to stable, nonhomeotropic phases. Coating glass slides with siloxanes has been shown to be an effective way of attaining homeotropic alignment for liquid crystalline materials, therefore, suggesting a possible explanation for the homeotropy observed in these phase separated siloxane copolymers[9] . These mesophases persisted up to 300°C, at which point observations were terminated. Some side chain thermotropic liquid crystalline systems have shown similarly wide mesophase regions[10], perhaps due to microheterogeneous phase separation as has been suggested by other workers in this field[10,11]

The general synthetic procedure for the preparation of these thermotropic rigid rod star-block copolymers suggests the preparation of a large number of new copolymers. Variations in both the star core and mesogenic types used could result in increased understanding of the role of topology and morphology in polymer liquid crystals.

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