Structuring of star-like multiarm polydimethylsiloxanes*

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The *in situ* structuring of multiarm star-like polydimethylsiloxanes (PDMS) synthesized on the base of the high-generation carbosilane dendrimers was studied. It was shown that, in contrast to the structures with 12, 16, and 48 arms, 128-arm star-like polydimethylsiloxanes form a stable mesophase formed by the PDMS arms. The data from polarized optical microscopy and differential scanning calorimetry revealed for the first time the formation of extended liquid-crystalline domains for the diorganosiloxane chains with the methyl substituents at the silicon atom. This effect can be attributed to the influence of close packing of the PDMS chains at the dendritic branching site in the case of actually multiarm structures.

Key words: polydimethylsiloxane, LC structures, multiarm polymeric stars.

It is known that the polydimethylsiloxane (PDMS) macromolecule is one of the most flexible among linear polymers.[1] Due to this, PDMS has a number of unique properties and is an important subject of the modern materials science. In contrast to other polydialkylsiloxanes, PDMS does not form columnar thermotropic structures.[2] However, it is known that the macromolecular chain in the closed space in the conditions of restriction of its molecular mobility shows special phase behavior. Change of molecular architecture of PDMS in star-like (12–48 arms) (see Ref. 3) or comb-like[4] structures does not affect the structuring; in neither case the formation of columnar mesophases was observed.

Anionic polymerization of hexamethylcyclotrisiloxane with a sixth-generation carbosilane dendrimer derivative as the initiator[3] afforded a series of star-like PDMS structures[4,5] with different number of arms (f) with the degree of polymerization 90 and higher.

Studies of 128-arm star-like PDMS by differential scanning calorimetry (DSC) and polarized optical microscopy (POM) allowed us to observe for the first time the formation of a stable mesophase formed by the PDMS arms. In contrast to compounds with the arm number $f = 12$, 16, and 48, for which no birefringent effect was observed in a wide temperature range up to the decomposition temperature, the stars with $f = 128$ form long liquid-crystalline domains at room temperature, which disappear at ~53 °C (Fig. 1). Note that this material is cloudy and non-flowing in contrast to other comb-like compounds based on PDMS. This is also an indirect evidence of the change in the morphology of the specimens.

It was shown by DSC that the phase behavior of the material with $f \leq 48$ is analogous to that of the linear PDMS: the heating curves contained a double melting peak at $T = -45$ °C (Fig. 2, curves *1* and *5*). At the same time, upon heating 128-arm star-like PDMS, an additional endothermic peak appeared at 53 °C (see Fig. 2, curves *3* and *4*) with the heat of melting typical of the transition from the liquid-crystalline mesophase to the isotropic state.

The nature of this transition was studied by small- and wide-angle X-ray scattering. A relatively wide reflex with the maximum at $2\theta = 11.49°$ was observed in the wide-angle diffusion region at room temperature in the samples of the star-like PDMS with $f = 128$ (Fig. 3, curve *1*). Note

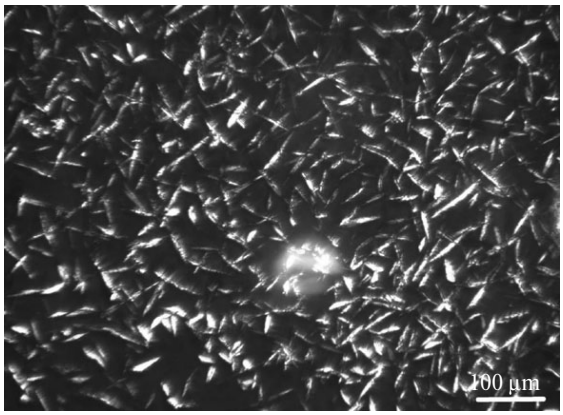

Fig. 1. POM image of the star-like PDMS with $f = 128$ at room temperature.

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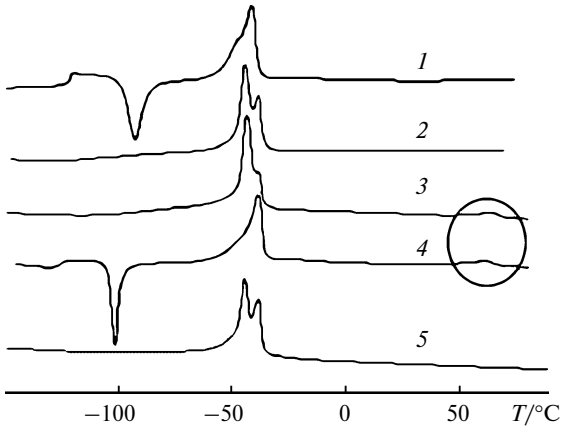

Fig. 2. DSC heating curves for the linear PDMS (*1*, *2*) and star-like PDMS with $f = 128$ (*3*, *4*) and $f \leq 48$ (*5*). Curves *1* and *4* were obtained upon heating the samples quenched in liquid nitrogen.

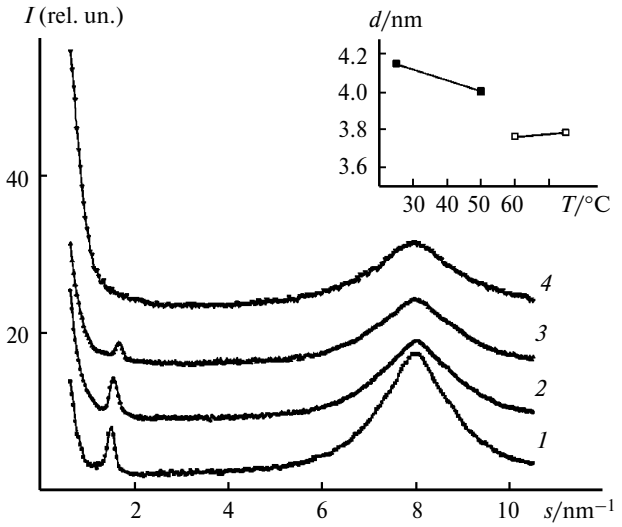

Fig. 4. Small-angle diffraction patterns for 128-arm PDMS at 25 (*1*), 50 (*2*), 60 (*3*), and 125 °C (*4*). The insertion shows the temperature dependence of the interlayer distance in 128-arm PDMS.

that a number of polydialkylsiloxanes with the side alkyl chain length of $n = 2$—6 carbon atoms are characterized by the formation of the rotary-crystalline two-dimensionally ordered hexagonal phase (Fig. 3, curves *2*—*5*) in contrast to compounds with longer lateral substituents ($n > 6$) (see Fig. 3, curves *6* and *7*). At the same time, no such phase has been observed earlier in polydimethylsiloxane. The reflex corresponding to the interlayer distance $d = 4.15$ nm was observed in the small-angle diffusion region (Fig. 4). Upon heating the samples to the phase transition temperature at 55 °C, its maximum was shifted to the wide-angle region ($d = 4.00$ nm, see Fig. 4, insertion). Subsequent heating results in a drastic decrease in the intensity and the disappearance of the small-angle reflex. One can assume that its presence is caused by the mutual ordering of the dendrimer nuclei into the smectic layered structures.

The ordering of long polydimethylsiloxane arms found in the present work is most likely due to the geometric constraints associated with the presence of the dendrimer nuclei and exerting the stabilizing role in the formation of the columnar mesophase. Note that the formation of the rotary-crystalline phase of PDMS requires provision of

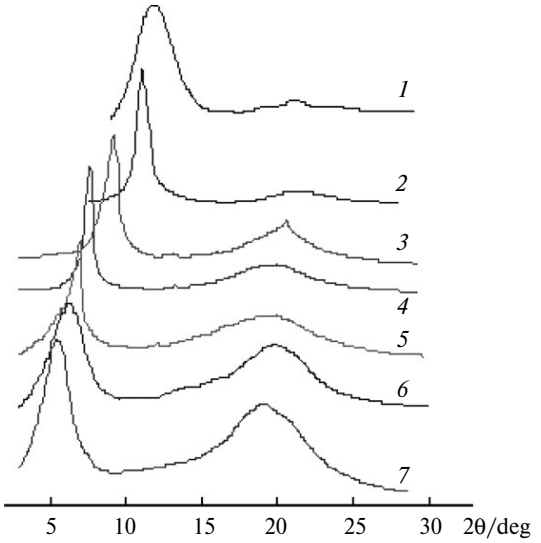

Fig. 3. Diffraction patterns for a number of polydialkylsiloxanes in the wide-angle diffusion region: *1*, 128-arm PDMS (300 K); *2*, polydiethylsiloxane (293 K); *3*, polydipropylsiloxane (373 K); *4*, polydipentylsiloxane (293 K); *5*, polydihexylsiloxane (300 K); *6*, polydiheptylsiloxane (293 K); *7*, polydinonylsiloxane (293 K).

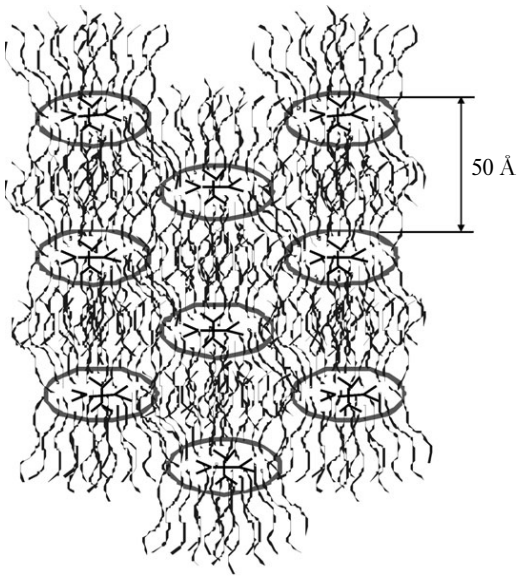

Fig. 5. Schematic view of the supermolecular structure formed by 128-arm star-like PDMS based on the sixth-generation carbosilane dendrimers.

a high concentration of arms linked with the dendritic core.[6] The smectic mesophase formed by the deformed nuclei fixes the position of the PDMS arms by maintaining their high density near the branching sites and, thereby, causing them to keep ordering within the temperature range where the smectic itself exists. The schematic view of the smectic and columnar mesophases is shown in Fig. 5.

Thus, we showed that long polydimethylsiloxane arms (with 90 $Si(CH_3)_2O$ units) of the star-like polymers with $f = 128$ based on carbosilane dendrimers possess a unique ability to form the rotary-crystalline mesophase in a wide temperature range.

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