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Effect of the method used for crystal structure formation on the rheological behavior of organocyclotetrasiloxane in the plastically crystalline state

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The rheological properties of *cis*-cyclotetrasiloxane, *cis*-$[PhSi(O)(OSiMe_3)]_4$, in the plastically crystalline state were investigated. The yield stress and non-Newtonian character of the flow indicates that *cis*-$[PhSi(O)(OSiMe_3)]_4$ is a viscoplastic material with respect to its rheological behavior. The conditions of crystal structure formation determine the rheological properties of organocyclotetrasiloxane in the mesophase. The temperature and stress during capillary flow were shown to affect the size and orientation of crystallites formed upon cooling of extrudates.

Key words: rheological properties, viscoplasticity, organocyclotetrasiloxane, crystal structure, plastic crystal.

This work is devoted to the rheological properties of organocyclosiloxanes in the 3D mesomorphic state, *i.e.*, in the plastically crystalline state. Such investigations are of interest, because the rheology of plastic crystals is not virtually studied. Only several works are known in which the shear rate of cyclohexane and adamantane plastic crystals was studied by uniaxial compression.[1] We pioneered to monitor the main regularities of the viscous flow of plastic crystals for the whole series of stereoregular organosiloxanes different by both lateral frame structures and cycle sizes. This study is possible due to the development of a new method for hydrolysis of trifunctional alkoxysiloxanes in the presence of alkali and transition metal ions. This method allowed us to obtain the whole class of new stereoregular mesomorphic organosiloxanes with tri-, tetra-, hexa-, octa-, and dodecasiloxane cycles,[2—9] some of which form the mesophase of the plastically crystalline type.[4,5,7,9] Before the beginning of our studies, only one organosiloxane was known that can form the mesophase of the plastically crystalline type, namely, octaphenylcyclotetrasiloxane.

In this work, we studied the rheological behavior of cyclotetrasiloxane, *cis*-$[PhSi(O)(OSiMe_3)]_4$, in the mesomorphic state and the dependence of the rheological characteristics of the cyclotetrasiloxane mesophase on the conditions of crystal structure formation affecting the crystal defectness. The purpose of this approach was to establish to which extent does the plastic crystal "remember" its crystalline pre-history after the "crystal→mesophase" transition?

Experimental

Cyclotetrasiloxane was prepared according to a previously described procedure.[4,5] According to the data of DSC, X-ray diffraction analysis, and polarization microscopy,[4,5,7] this compound forms the mesophase of the plastically crystalline type in the 80—242 °C temperature interval and is sublimed with the further temperature increase.

Three cyclotetrasiloxane samples obtained under different crystallization conditions were prepared: the first sample (**1**) was obtained upon fast crystallization of cyclotetrasiloxane from a saturated solution in 95% EtOH, the second sample (**2**) was slowly crystallized from a dilute solution in 95% EtOH, and the third sample (**3**) was obtained by sublimation *in vacuo* (1 Torr) at 240—260 °C.

Rheological studies were carried out on an MV-2 capillary microviscosimeter[10] using a capillary 2.09 mm in diameter and 10 mm long. Diffraction patterns and X-ray photodiffraction patterns were obtained in the transmission regime on a Dron-3M diffractometer and an IRIS-3.0 setup (CuKα). Temperatures and heats of phase transitions were determined by the DSC method (Mettler, TA-4000).

Results and Discussion

The flow of crystalline substances and plastic crystals occurs due to crystal defects: vacancies and disloca-

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tions*.[1,11] The mechanical properties of crystals, strength, and plasticity are caused, to a great extent, by dislocations and their motion. The dislocation motion during plastic flow is prevented by the strength of cleaved interatomic bonds, elastic interaction with other dislocations, intergrain boundaries in polycrystals, and other defects in crystals. A portion of the work of external forces is consumed to surmount these hindrances. Thus, both classical and plastic crystals with dislocations become "softer" than their defectless analogs.

The defectness of crystal can be substantially changed by the variation of conditions of crystal structure formation. Therefore, taking into account the identity of flow mechanisms in classical and plastic crystals, we can establish the "inheritance" of defects introduced into a crystal by the plastic crystal after the "crystal→plastic crystal" thermotropic phase transition.

To solve this problem, we prepared three cyclotetrasiloxane samples obtained under different crystallization conditions (see Experimental). Different defects of the crystalline phase were confirmed by the DSC and X-ray diffraction data (Fig. 1). In fact, the melting point of the crystalline phase in sublimed sample **3** is somewhat lower than that in sample **2** (see Fig. 1, *a*). A more perfect crystal structure of sample **2** is also indicated by the higher enthalpy of melting compared to that of sample **3** (see Fig. 1, *a*).

The powder diffraction patterns of the cyclotetrasiloxane samples (see Fig. 1, *b*) indicate that their crystalline lattices are identical. However, the diffraction patterns show that the lowest defectness of the crystal structure is inherent in sample **2**, while sample **3** is characterized by the highest defectness (see Fig. 1, *b*). An increase in the defectness of the structure is indicated by broadening of the reflections and a decrease in their intensity with an increase in the scattering angle.

Viscous flow of cyclotetrasiloxane becomes possible after the crystal→mesophase phase transition and covers the temperature interval from 80 to 240 °C, *i.e.*, almost to the beginning of material sublimation. For all three samples, the flow process begins only after the shear stress exceeding the yield stress ($\tau_{\text{y.s.}}$) of the material has been achieved. It is difficult to experimentally determine $\tau_{\text{y.s.}}$ because of very low stress rates and slow achievement of the established flow regime. Therefore, the $\tau_{\text{y.s.}}$ value was determined using the Casson equation[12]

$$\tau^{1/2} = \tau_{\text{y.s.}}^{1/2} + (\eta D_{\text{r}})^{1/2},$$

where τ is the shear stress, η is the viscosity, and D_{r} is the shear rate.

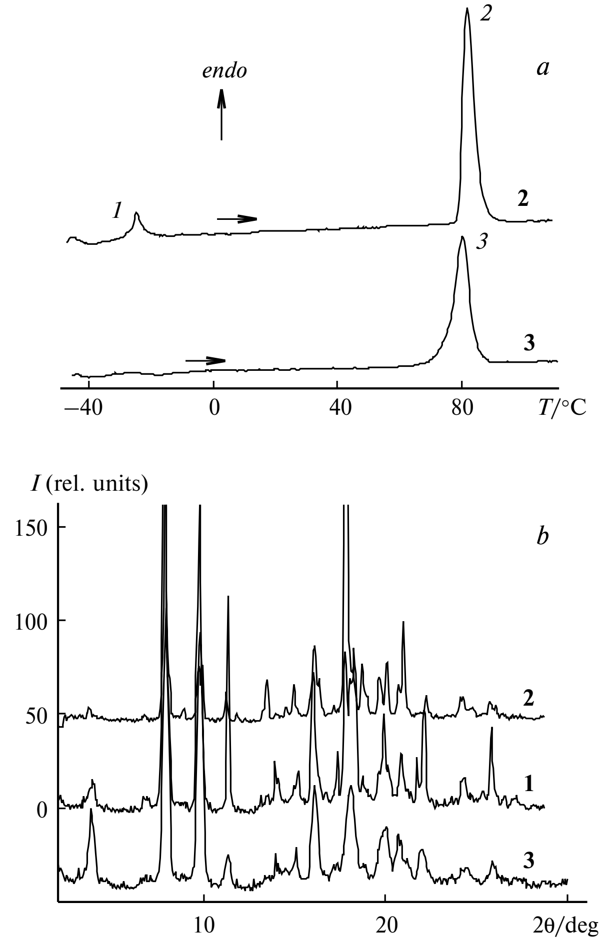

Fig. 1. DSC curves obtained upon heating (*a*) and diffraction patterns (*b*) of samples **1**—**3**. The cyclotetrasiloxane samples were obtained by fast (**1**) and slow (**2**) crystallization from 95% EtOH and by sublimation (**3**).

Peak	T/°C	ΔH/kJ g^{-1}
1	−24	2.9
2	83	26.4
3	80	21.9

The temperature plots of $\tau_{\text{y.s.}}$ are presented in Fig. 2. At 80 °C, the sample obtained by slow crystallization is characterized by the highest $\tau_{\text{y.s.}}$ value, while this value is the lowest for the sublimed sample. The $\tau_{\text{y.s.}}$ value decreases with the temperature increase and is almost equal for all samples at 200 °C. It should be noted that the run of the temperature plot of $\tau_{\text{y.s.}}$ for plastic crystals is similar to the analogous plots for metals and alloys.[13]

The flow curves of the cyclotetrasiloxane samples in the plastically crystalline state at different temperatures are presented in Fig. 3, *a*—*c*. The character of the flow curves and apparent viscosity (η_{app}) depend on the conditions of crystal structure formation. The fact that the viscosity also depends on the applied stress indicated the non-Newtonian character of flow for these materials. Only

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* Dislocations are lines along and near which the regular arrangement of atomic planes, being characteristic of crystal, is distorted.

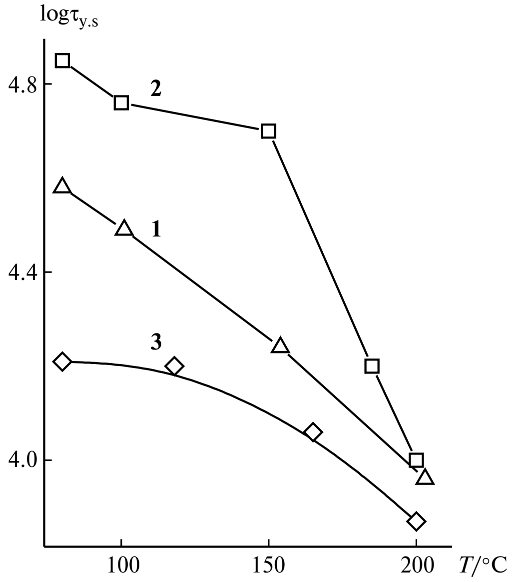

Fig. 2. Temperature plots of the yield stress for the cyclotetrasiloxane samples obtained by fast (**1**) and slow (**2**) crystallization from 95% EtOH and by sublimation (**3**).

some flow curves are linear (see Fig. 3, *b*) and can be described by the equation $\eta = D_r^{n-1}$, where n is the flow index. For example, for sample **1** tested at 80 and 200 °C, the n flow index is equal to 0.2, which is substantially lower than n for Newtonian fluids but is typical of the flow of viscoplastic materials.[14,15] The existence of the yield stress and non-Newtonian character of the flow make it possible to attribute plastic crystals to viscoplastic materials by the character of their rheological behavior.

The apparent viscosity values calculated at the shear stress constant for each series were used for plotting the temperature dependence of the viscosity in the Arrhenius coordinates (Fig. 4). The temperature plots of the viscosity are straight lines, which makes it possible to calculate the apparent activation energy (E_a) for all samples using the equation

$$\eta = Ae^{E_a/RT},$$

where R is the universal gas constant, and T is the temperature (K).

For the samples obtained by crystallization from solutions, the E_a values are almost the same (72—73 kJ mol^{-1}), while E_a of the sublimed sample is much lower (44 kJ mol^{-1}).

The following fact is of interest. After the material leaves the capillary, extrudates of the samples obtained by different methods do not always transit to the crystalline state on cooling to room temperature, *i.e.*, the rate of the "mesophase→crystal" transition is also related to the method of sample preparation. For example, extrudates of the samples obtained by crystallization from solutions are crystallized (become turbid) within several minutes, whereas the sublimed sample remains transparent (mesomorphic) for more than a day.

The X-ray photodiffraction patterns of the extrudates obtained at different temperatures from samples **2** and **3** are presented in Fig. 5. The extrudates are characterized by the oriented polycrystalline structure (the crystal structure is identical), and the orientation and crystallite size depend substantially on the sample type and extrusion temperature T_{ext}. The largest crystallite size ($\lambda \gg 1000$ Å) is observed for sample **2** at T_{ext} = 150 °C. When T_{ext} of sample **2** increases to 200 °C, the crystallite sizes decrease substantially ($\lambda \ll 1000$ Å); the good predominant orientation of the crystallites is retained. The extrudate obtained from sample **3** at

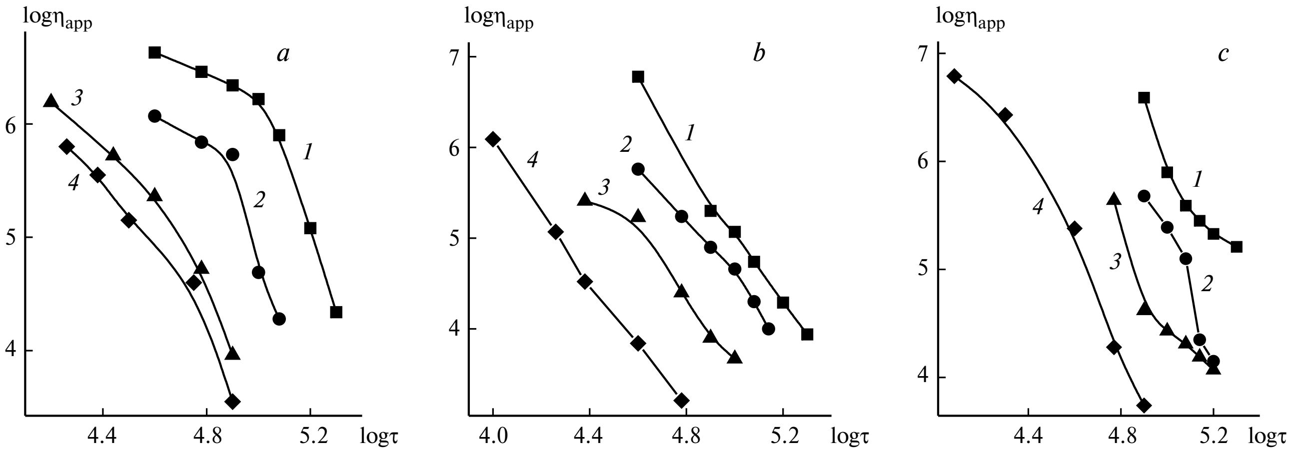

Fig. 3. Flow curves of the cyclotetrasiloxane samples obtained by sublimation (*a*), fast (*b*) and slow (*c*) crystallization and tested at temperatures 80 (*1*), 100 (*2*), 150 (*3*), and 200 °C (*4*).

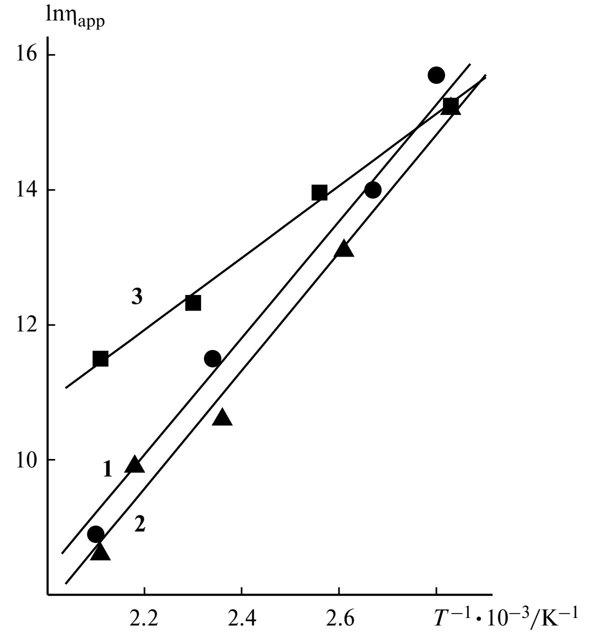

Fig. 4. Temperature plots of the apparent viscosity of the cyclotetrasiloxane samples obtained by fast (**1**) (τ = 40 kPa) and slow (**2**) (τ = 80 kPa) crystallization from 95% EtOH and by sublimation (**3**) (τ = 40 kPa).

T_{ext} = 92 °C consists of fine crystallites, and the orientation of the crystallites is lower than that for extrudate **2** obtained at T_{ext} = 200 °C. An increase in T_{ext} for sample **3** to 200 °C leads to the formation of an extrudate with the very weakly pronounced orientation of crystallites. All these facts indicate indirectly that each sample is inherent in specific features of the flow in the mesomorphic state. These specific features are related mainly to the sample morphology, which can be simulated in the crystalline state.

The pre-history of crystal structure formation of the cyclotetrasiloxane samples exerts a substantial effect on their rheological properties in the mesophase (yield stress, apparent viscosity, activation energy of flow). Slow crystallization favors the formation of a less defect crystal structure, which is retained after the thermotropic transition to the orientationally disordered 3D mesomorphic state (to the plastic crystal). Using different procedures of crystallization, one can purposefully affect the rheological properties of materials in the plastically crystalline state and on the morphology of the extrudate obtained after cooling down from the extrusion temperature. The extrudate morphology (orientation and crystallite size) also depend substantially on the extrusion conditions (temperature, applied load, *etc.*).

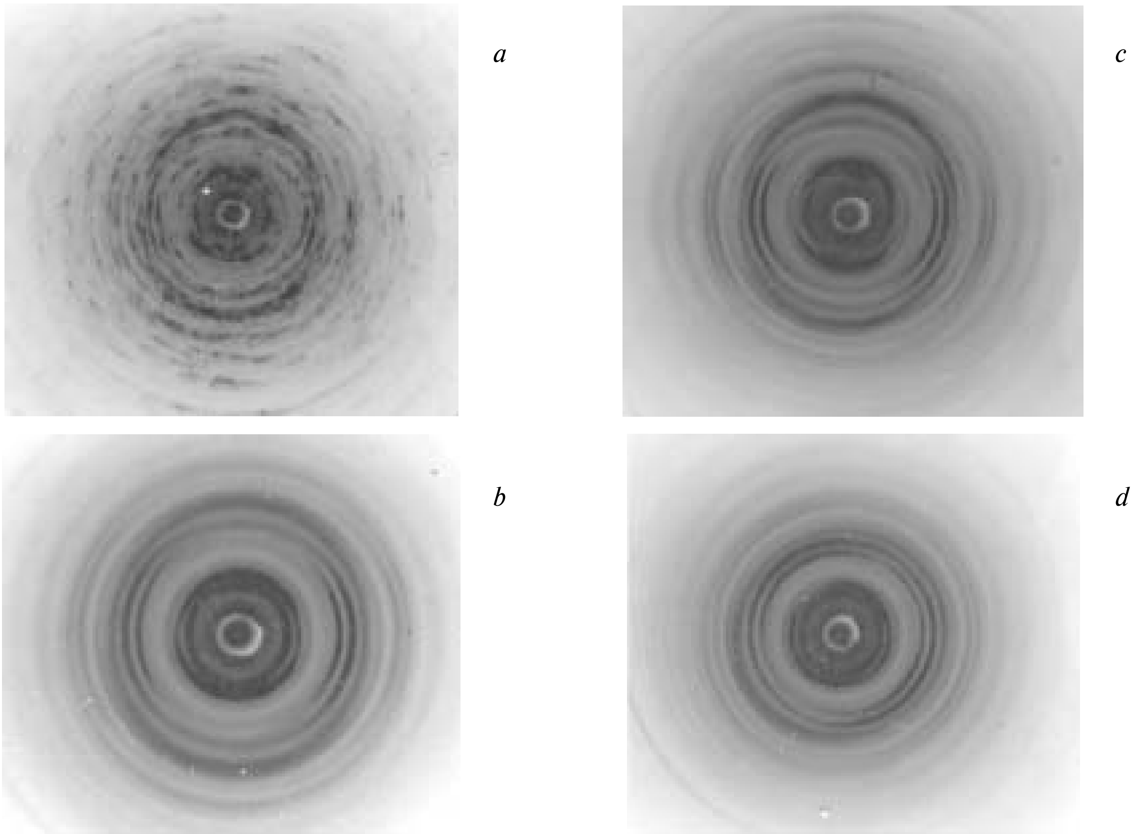

Fig. 5. X-ray photodiffraction patterns of the extrudates obtained from the samples by slow crystallization (*a*, *b*) and sublimation (*c*, *d*) at different temperatures: *a*, 150 °C (τ = 0.16 MPa); *b* and *d*, 200 °C (τ = 0.12 MPa); *c*, 92 °C (τ = 0.16 MPa).

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