THE STRUCTURE OF POLY(SILYLENEMETHYLENE)S

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The structure of poly(di-*n*-alkylsilylenemethylene)s (alkyl=ethyl to hexyl) and side chain liquid crystalline poly(silylenemethylene)s (-($SiCH_3R$-CH_2)- : R=$O(CH_2)_N$O-Ph-Ph, Ph; phenyl) (PSM-N; N=3,6,8,11) have been studied using X-ray, electron diffraction, differential scanning calorimetry (DSC) and polarized optical microscopy. The backbone conformation of each of these poly(di-*n*-alkyl-silylenemethylene)s is all-*gauche*, giving them a 4_1 helical structure. All studied poly(di-*n*-alkylsilylenemethylene)s except poly(di-ethylsilylenemethylene) (PDESM) have similar packing with a two dimensional monoclinic *ab*-projection of the unit cell containing one chain. PDESM with the shortest alkyl side chain, has a pseudo-hexagonal unit cell containing two chains (four repeat units), one at the corner and the second nearly in the center of the *ab*-projection of the unit cell. The length of the alkyl side chains affects the packing without changing the backbone conformation. The chains with all-*gauche* conformation in the backbone and all-*trans* conformation in alkyl side chain are well packed in these unit cells. The calculated electron diffraction patterns are well matched with the experimentally observed ones.

All PSM-Ns studied show a series of sharp equatorial reflections in the X-ray fiber pattern at room temperature, a characteristic of well-ordered smectic phases. Layered smectic structures of PSM-Ns persist up to the isotropic temperature during heating, although the specific kinds of smectic phases changed. In each, the layer thickness corresponds to the single side chain length and increases with slope of ~1.3 Å per a methylene spacer. This is a single-layer structure. For PSM-3 and PSM-6, the mesogens pack in a two-dimensional orthorhombic cell, a characteristic of a smectic E (S_E) phase, with dimensions *a*=8.14Å and *b*=5.14Å. The S_E phase of PSM-3 and PSM-6 converts directly to the isotropic phase. For PSM-8 and PSM-11, the mesogens pack in a hexagonal smectic B (S_B) cell at room temperature. This is manifest from the hexagonal six-point arrangement of reflections at d=4.4Å in the X-ray fiber pattern. During room temperature annealing, PSM-8 and PSM-11 crystallize into orthorhombic cells with parameters *a*=8.8Å, *b*=5.08Å, *c*=50.8Å for PSM-8 and *a*=8.90Å, *b*=5.14Å, *c*=58.6Å for PSM-11. Upon heating, the crystalline structures change to smectic A (S_A) before becoming isotropic. Micrographs of PSM-11 show a layered structure with thickness matching that observed in X-ray pattern.