

Surface-induced organization of linear molecules on nanostructured polytetrafluoroethylene: Crystalline state of poly[vinylidene fluoride-trifluoroethylene]

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Highly crystalline and uniaxial-oriented polytetrafluoroethylene films, nanostructured in one dimension, were used to produce a fully crystalline, thermoreversible morphology in the ferroelectric copolymer poly[vinylidene fluoride-trifluoroethylene]. The resulting state is built up of regularly stacked lamellar crystals of about 100 nm thickness and lateral dimensions of about 6 μm . [S0163-1829(97)00202-6]

INTRODUCTION

Because of intramolecular disorder, large molecular chain length and chain length distribution polymers do not usually form macroscopic single crystals, but do partially crystallize at best.¹ Exceptions are, e.g., polydiacetylenes, which can be prepared as macroscopic monomer single crystals and polymerized by uv irradiation (e.g., Ref. 2) afterwards.

Recently, Wittmann and Smith³ have demonstrated that ultrathin highly oriented films of polytetrafluoroethylene (PTFE) obtained by rubbing a PTFE rod on a glass substrate are able to organize very different types of linear molecules. The organization of these different materials has in common that their linear molecular chain axes direct themselves along the rubbing (friction) direction of the PTFE, i.e., along the direction of the PTFE molecules. Although the organization mechanism is not well understood yet,^{3,4} this technique, in the following denoted as PIA technique (PTFE induced alignment), has been very successfully used to organize materials like liquid crystals,^{5,6} single crystals of linear molecules,^{7,8} and several partially crystalline polymers^{9,10} within their natural state.

The crystalline room-temperature phase of PTFE is hexagonal, built up from 15₇ helices with lattice parameters $a = b = 0.556$ nm and $c = 1.95$ nm.¹¹ According to Fenwick, Smith, and Wittmann,¹² the crystalline morphology of the PTFE on its glass substrate is as follows: the preferential molecular chain direction (c axis) is in the plane of the glass substrate along the friction direction, the (b, c) plane being the contact plane.

In order to prove the power of the PIA method, we have chosen the ferroelectric statistical copolymer poly[vinylidene fluoride-trifluoroethylene] P(VDF/TrFE)

with 70 mol % vinylidene fluoride and 30 mol % trifluoroethylene (subsequently denoted as P73) as a model system. The aim of this paper is to show that a combination of the PIA method and a modified Bridgman process yield for P73 a thermoreversible crystalline state with a surface-induced morphology which leads to outstanding physical properties. Structural, optical, acoustic, and electrical investigations indicate the existence of a highly oriented state built up of rather regularly stacked crystalline lamellae with a vanishing degree of amorphicity. Results on the spatial decay of the global order are presented. The determination of the optical properties is possible using a technique based on the ΘR -Brillouin scattering technique.¹³ The natural counterpart of this highly structured material is the usual semicrystalline P73 as obtained from solution or melt. At ambient temperature natural P73 is semicrystalline with a typical degree of crystallinity of about 70%. Our P73 had an average molecular weight of $M_w = 300\,000$ g/mol with a typical polydispersity $M_w/M_n \approx 2$ (Ref. 14) and a mass density $\rho = 1885$ kg/m³ estimated from a pycnometer measurement.

The ferroelectric low temperature phase (usually denoted as β phase) has the space group $Cm2m$ and consists of the polymer chains in almost all-trans conformation^{15,16} with two monomer units per unit cell. Conventionally, the crystallographic c axis and b axis are taken along the molecular chain axis and the direction of the ferroelectric spontaneous polarization P_s , respectively. For the ferroelectric single crystal a spontaneous polarization of $P_s = 0.11$ C/m² was predicted.¹⁷ Due to the semicrystalline morphology, the crystallites are usually embedded in their amorphous matrix with their crystal axes oriented at random. This random morphology is responsible for the typical viscoelastic properties of polymers, but is unfavorable for most applications based on the crys-