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The Polymorphism of Poly(vinylidene fluoride)

V. The Effect of Hydrostatic Pressure on the Melting Behavior of Copolymers of Vinylidene Fluoride*

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Summary

The high-pressure melting behavior of samples of vinylidene fluoride copolymerized with vinyl fluoride, trifluoroethylene, or tetrafluoroethylene indicate that the copolymers have a lower entropy of melting than the poly(vinylidene fluoride) homopolymers in the same phase. As the comonomer size increases, the entropy of melting decreases. High-pressure crystallization of copolymers of 91-9 mole% vinylidene fluoride-trifluoroethylene and 93-7 mole% vinylidene fluoride-tetrafluoroethylene results in a high-melting form of phase I (planar zig-zag).

INTRODUCTION

The effect of elevated hydrostatic pressure on the crystal structure, morphology, possible polymorphism, and physical properties of macromolecules has become the subject of intensive study within the past 15 years.

Wunderlich and Arakawa [1] and Geil et al. [2] demonstrated that upon pressure-crystallizing polyethylene (PE), they were able to obtain extended-chain crystals in the bulk rather than the normal folded-

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chain morphology. Holdsworth and Keller [3] observed that a small amount of the triclinic form of PE originally suggested by Turner-Jones [4] was present in samples which were pressure crystallized at 4000 atm. High-pressure differential thermal analysis (DTA) studies have been performed on both folded-chain and extended-chain PE crystals from 1 to 4000 atm [5]. These high-pressure DTA studies indicated that the extended-chain crystals melt at a higher temperature than the corresponding folded-chain crystals at the same pressure, as is suggested by theory [6].

High pressure would appear to be a promising method of preparing new polymorphic forms of polymers with differing unit cells and chain conformations. In addition to the polymorphic forms of PE discussed above, the rate of transformation of polybutene-1 from form II to form I has been found to increase as a function of pressure [7,8]. The γ form of polypropylene results from crystallization at 5000 atm. This polymorphic form of the polymer is not commonly found after crystallization at atmospheric pressure [9-11]. Polytetrafluoroethylene (PTFE) undergoes several solid-solid polymorphic transitions when subjected to varying thermal and elevated pressure conditions [12-19]. Several studies have been made on the effect of pressure on the melting behavior of PTFE [18,19].

The homopolymer of poly(vinylidene fluoride) (PVF_2) exhibits at least two polymorphic phases under atmospheric conditions [20-26]. Head-to-head linkages play a large role in determining which phase will form upon crystallization. Crowding along the chain for phase II becomes more severe with increasing head-to-head content, whereas crowding decreases with increasing head-to-head content for phase I [21]. Nuclear magnetic resonance (NMR) studies have demonstrated that PVF_2 normally contains 5-6% head-to-head linkages immediately followed by tail-to-tail linkages [27-29]. Phase I of PVF_2 has been shown to have a planar zig-zag chain conformation and an X-ray crystalline density of 2.0 g/cc [7]. Phase II of PVF_2 has a trans-gauche-trans-gauche' chain conformation with a crystalline density of 1.90 g/cc [22,30]. When PVF_2 is pressure-crystallized at 280°C and 5000 atm, it has been previously shown [31] that a mixture of phase II with a melting point of 160°C and a planar zig-zag phase with an increased melting point of 187°C resulted. The samples crystallized under these conditions consisted mainly of the planar zig-zag form. As the degree of supercooling was increased, the amount of phase II increased. If samples of the high-pressure crystallized PVF_2 were oriented, then the remaining phase II was converted to the high-melting planar zig-zag form. Doll and Lando had originally designated as phase III the material which resulted from the high-pressure crystallization of PVF_2 .