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Effect of molecular weight and chain end groups on crystal forms of poly(vinylidene fluoride) oligomers

Herman, Toshiyuki Uno, Astushi Kubono, Susumu Umemoto, Takeshi Kikutani and Norimasa Okui*

Tokyo Institute of Technology, Department of Organic and Polymeric Materials, Ookayama, Meguroku, Tokyo 152, Japan

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The micro-structure of poly(vinylidene fluoride) oligomers was characterized by ^{19}F and ^{13}C n.m.r. and the effects of molecular weight and the chain end groups on the crystal forms were studied by i.r. and X-ray methods. One of the oligomers terminated with $-CH_3$ and the fragment of an initiator at the chain ends. The other oligomers were terminated with $-Cl$ and CCl_3- at their chain ends. The larger chain end groups tended to produce the conformational disorder in the molecules yielding the γ form. The smaller molecular weight of the oligomer gave rise to the β form. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(vinylidene fluoride); oligomer; chain end)

INTRODUCTION

The crystal form of poly(vinylidene fluoride) (PVDF) can be divided into roughly three forms: α, β and γ. The β and the γ forms of PVDF exhibit piezoelectricity, but not the α form[1]. In general, the α form can be obtained by crystallizing PVDF from the melt or by casting from acetone solution. The β form can be obtained by drawing and poling PVDF film or by quenching the film from the molten state[2]. The γ form can be prepared by annealing the film at a relatively high temperature.

PVDF is thermally decomposed in a vacuum system when the polymer is heated above 300°C. Low molecular weight fractions (oligomers) in PVDF can be evaporated without thermal decomposition at temperatures below 300°C[3,4]. The molecular weight of VDF oligomers obtained by vapour deposition depends on the deposition conditions, such as evaporation crucible temperature, pressure, distance from the source crucible to the substrate, etc. The molecular orientation and the crystal structure in the films could be controlled by the substrate temperature and the deposition rate[5]. For example, VDF oligomer deposited at substrate temperatures below −100°C yields the β form with the molecular orientation parallel to the substrate. The α form is obtained at a substrate temperature of 25°C with the normal molecular orientation to the substrate.

In this study, we present the characterization of the oligomers obtained from the vapour deposition method and those prepared by telomerization of VDF monomer in the presence of CCl_4. The effects of molecular weight and the chain end groups on the crystal form, α, β and γ, are studied by i.r. and X-ray methods.

* To whom correspondence should be addressed

EXPERIMENTAL

Samples

Poly(vinylidene fluoride) (PVDF) and three VDF oligomers (A, B and C) were used in this study. PVDF was a commercial sample purchased from Showa Denko Co. Ltd with molecular weight of 88 000. One of the VDF oligomers (sample A) was accumulated from PVDF by the vapour-deposition method at below 300°C where the low molecular weight fractions in PVDF were evaporated without thermal decomposition[3,4]. The other VDF oligomers of B and C samples were kindly supplied from Kureha Co. Ltd. where VDF monomers were telomerized by suspension polymerization method in acetone solution in the presence of CCl_4 with di-*n*-propyl-peroxy-dicarbonate as a catalyst.

Measurements

Solution-state ^{19}F and ^{13}C n.m.r. were recorded on a JEOL JMN-GX 500 spectrometer operating at 245.05 and 125.65 MHz, respectively. ^{13}C n.m.r. was measured in broad-band proton decoupling mode. Samples were dissolved in acetone-d_6 (99% purity). X-ray diffraction patterns were recorded with a conventional $\theta - 2\theta$ diffractometer (Rigaku Rad-B). I.r. spectra of the samples were recorded by JASCO Micro F.T.i.r. 100T. Melting and crystallization temperatures for the samples were recorded on a Shimazu T40 at a heating rate and a cooling rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows ^{19}F n.m.r. spectra for PVDF and two oligomers of A and B. According to the reference data