Influence of molecular weight on the crystallization of poly(vinylidene fluoride)

Enzo Benedetti[1,*], Aldo D'Alessio[1], Claudio Bertolutti[1], Piergiorgio Vergamini[1], Natalino Del Fanti[2], Maurizio Pianca[2], and Giovanni Moggi[2]

[1]Dipartimento di Chimica e Chimica Industriale, Via Risorgimento, 35, I-56126 Pisa, Italy
[2]Montefluos C.R.S., Via S. Pietro, 50, I-20021 Bollate, Italy

Abstract

Five samples of Poly(vinylidene fluoride) with a molecular weight from 45,000 to 260,000 were analyzed by means of FT-IR spectroscopy in order to study the influence of molecular weight ($\bar{M}v$) on the crystallization process. The spectra of films obtained from methylethylketone solutions revealed the prevalence of form II (α) in the case of lower $\bar{M}v$ and of form III (γ) in the higher molecular weight samples. The amount of form III was found to increase as the Mv decreased and as annealing temperatures increased. The deconvolution technique of vibrational spectra allowed detection of small amounts of other forms accompanying the prevailing one.

Introduction

Poly(vinylidene fluoride)(PVDF) can exist mainly in three crystalline modifications denoted as I(β)(orthorombic),II(α)(pseudo orthorombic) and III(γ)(monoclinic) in which the chains assume the conformation TTTT, TGTG' and TTTGTTTG', respectively[1,2].Two additional forms IV(ε)and V(α_p) have recently been evidenced by means of X-ray diffraction[3,4].
The transformation of one form into another can be achieved by thermal[5], mechanical[6], or electrical[7] treatment.
The features of the vibrational spectra of PVDF have attracted a great deal of interest since 1961, and certain infrared absorptions,[1,8,9,10] characteristic of the different polymorphous forms, have been extensively employed in the study of the crystallization process. One of the major aims, from the vibrational point of view, is to obtain the infrared spectra corresponding to each pure crystalline form. The spectra of the three most common crystalline forms were obtained by subtracting the spectra of unannealed samples from those of annealed samples, variously prepared in order to obtain the three forms[2].
Crystal phase transformation relative to the passage from form II(α)to form I(β) at variable temperatures has recently been investigated by simultaneous FT-IR and stress-strain measurements.[11]
Transformation from the helical II(α) phase to the one containing trans sequences, i.e. those present either in phase I(β) or III(γ) can be obtained quite easily when PVDF is exposed to an electric field[7].
Crystallization from different solvents such as dimethylsulphoxide[12], dimethylacetamide(DMA), methylethylketone (MEK)[9], dimethylformamide, and monochlorobenzene[1] gives different polymorphic forms.
The different degree of tail-tail (-CH2-CH2-) sequences also plays a very

important role in the crystallization of the polymer and in determining the nature of its properties. For instance, form I is more stable than form II within the 11-14% defects range,[13] while form II appears to be more stable below 11% defects[13] and in the vicinity[14] of 20%.
Some discrepancies found in literature between the infrared spectra of films obtained by casting solutions from different solvents might be related to a different reverse addition content, to the use of samples with different molecular weights, or to the examination of commercial products lacking in high purity.
Despite the large number of infrared and Raman investigations carried out on the various phases of PVDF, no vibrational data concerning the influence of the molecular weight on crystal transformation are yet available.
This paper reports the results of an investigation carried out using FT-IR spectroscopy on PVDF samples of different molecular weights in order to study the influence of this parameter on the crystallization of non-oriented samples. All our PVDF samples examined by means of NMR, showed the same content of reverse addition (about 3%).

Experimental

The five PVDF samples investigated (Tab.1), were synthetized by soapless emulsion polymerization with ammonium persulphate initiator (T=85-95°C, P=6-12 atm).
The polymers were coagulated by pouring them into a stirred 10% hydrochloric acid solution, washed with demineralized water and dried at 50°C under a vacuum for 6 hrs.
Molecular weights were determined from the intrinsic viscosity in DMA solutions[15].
The amount of reverse addition was calculated by means of 19F NMR spectroscopy, using a Varian XL-200 spectrometer operating at 188.22 MHz.
Films were obtained by casting solutions in MEK previously dried and distilled.
Annealings were carried out by heating the samples up to 210°C to destroy crystalline residues and then keeping the films at 120,130,145 and 165°C for 20 hrs.
Infrared spectra were obtained using a Perkin-Elmer FT-IR mod.1750 spectrometer.One hundred scans of 2 cm^{-1} resolution were signal-averaged.

TABLE 1 Intrinsic viscosity and molecular
weight ($\bar{M}v$) of the PVDF samples
examined

Intrinsic Viscosity (dl/g)	Molecular[15] Weight ($\bar{M}v$)	Reverse Addition (%)
0.28	45,800	3.0
0.55	124,540	3.1
0.66	162,000	3.1
0.81	220,000	2.9
0.90	258,300	3.0

Results and discussion

All the PVDF samples listed in Tab. 1 ,with a molecular weight ranging from about 45,000 to 260,000, were examined by means of FT-IR spectroscopy.From all the spectra, run on films obtained by casting solutions in MEK or on samples in KBr matrices, those characteristic of forms I,II and III on the basis of previous assignments[1,2,10] are compared in Fig.1.
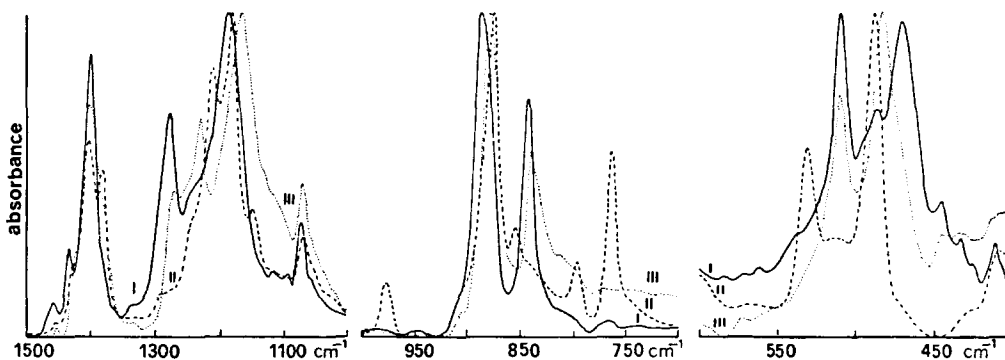

Fig.1 FT-IR spectra of PVDF: form I(—), form II(---), and form III(···)

This picture, in which the positions and intensities of the bands characteristic of the three forms are compared, is lacking in literature, and may prove to be useful in determining the presence of more than one form as well as the purity of the sample. The spectrum of each form was obtained by subtracting from the spectrum of a prevailing form those corresponding to the other two crystalline modifications. While the spectrum of form II is easily identifiable, those corresponding to forms I and III, show less noticeable differences because of their similar structures. In spite of the spectral differences observed mainly in the 1350-1150,950-800,and 550-450 cm^{-1} regions for forms I and III, the identification of one of these phases becomes very difficult when they are both present in a sample. The 550-450 cm^{-1} range seems to be the most suitable for the identification of these forms. The bands at 532 and 471 cm^{-1} are characteristic of the helical conformation TGTG (II or α) and of the planar zig-zag structure (I or β), respectively.The lack of these bands and the presence of absorptions at 511 and 484 cm^{-1} generally indicate the presence of form III. It is not easy to detect small amounts of this last form when form I is present in this region. In the presence of more than one form, the self-deconvolution technique may be useful to gain further information with regard to the number,position and relative intensity of the various components in the spectrum[16].For instance Fig.2 clearly shows, together with form II, the presence of form III, because of the component at 484 cm^{-1}.The application of this technique may prove to be extremely useful in order

to follow the transformation process from one phase into another, and to establish the purity of a form.
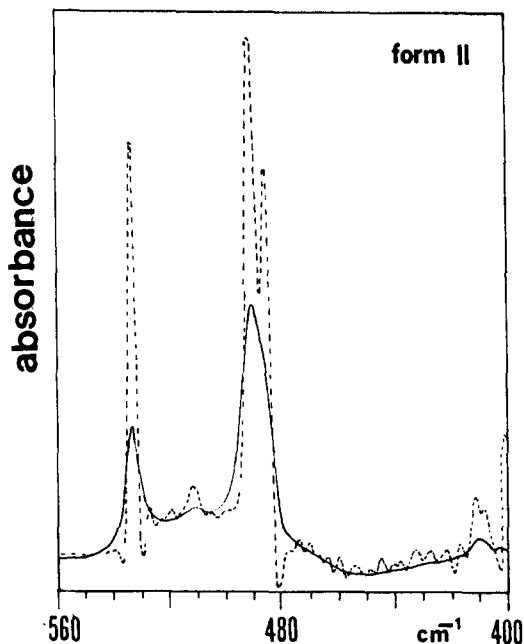

Fig.2 Normal (—) and deconvolved (---) FT-IR spectra of form II.

An examinination of films of PVDF samples with different molecular weights, obtained by casting solutions of MEK, shows that form II prevails in the low molecular weight samples, while form III is mainly present in the spectra of the higher molecular weight fractions.(Fig.3a) By analyzing the original samples in nujol or in KBr matrix (Figs. 3b,3c) without grinding the samples, forms II and III are both found to be present for the entire range of the molecular weights examined. Analysis of ground PVDF samples in KBr in agate mortar shows that form I always prevails independently of the molecular weight (Fig.3d). Temperature is known to have a strong influence on the polymorphism of PVDF. The growth of form III crystallites from the melt is favoured from 165°C to 180°C, while the development of form II is favoured below 165°C. At lower temperatures, the growth of form III crystallites is extremely slow, and hence a specimen quenched from the melt only shows a trace amount of form III under infrared spectroscopy[17]. These conclusions are in agreement with those of a recent paper in which the crystallization of PVF2 was studied employing a low electric field[7].
In order to gain further indications about the influence of temperature on the crystallization of PVDF, all the samples were heated at 210°C for ten minutes in order to destroy completely crystallinity, and then they were annealed at 120, 130, 145, and 165°C as shown in Figs.

4a,4b,4c,4d. Form III prevails for low and medium molecular weights, while for higher molecular weights the absorptions of form II are found to be more intense. At the annealing temperature of 165°C, the maximum purity of forms II and III is reached for the higher and lower molecular weight respectively.
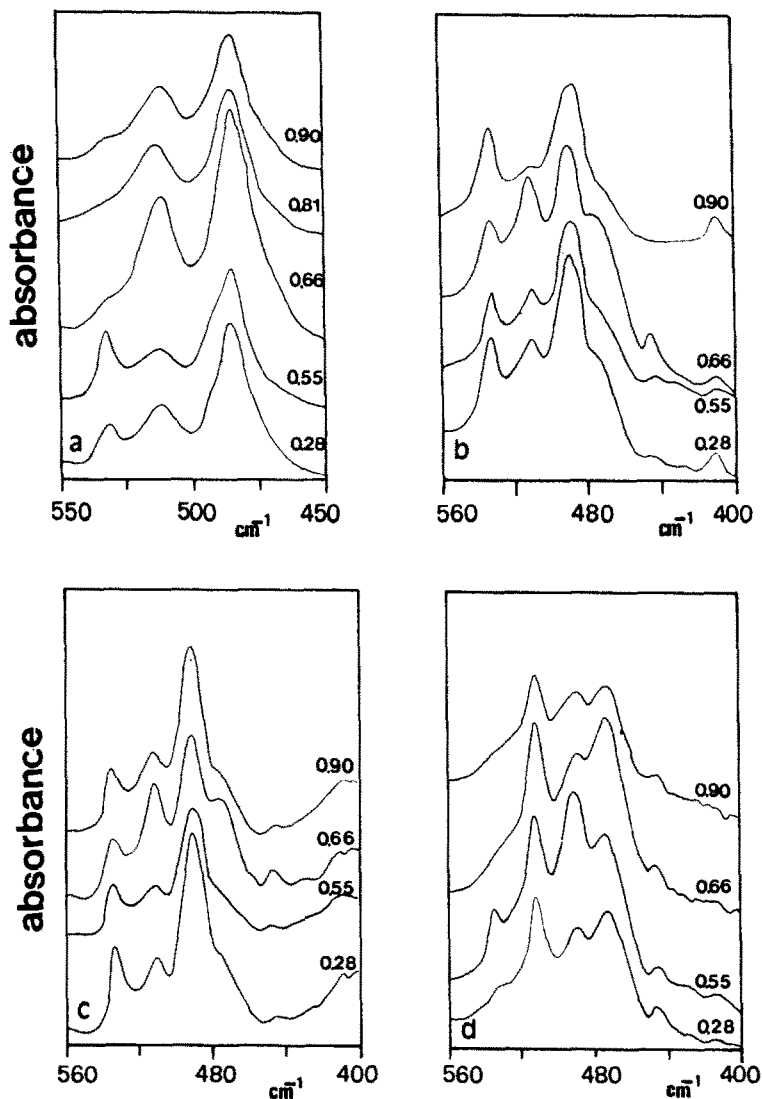

Fig.3   FT-IR spectra of PVDF samples with different intrinsic viscosity: films obtained from MEK solution (a); samples in KBr matrix (b); samples in Nujol (c); samples strongly grinded in KBr matrix (d).
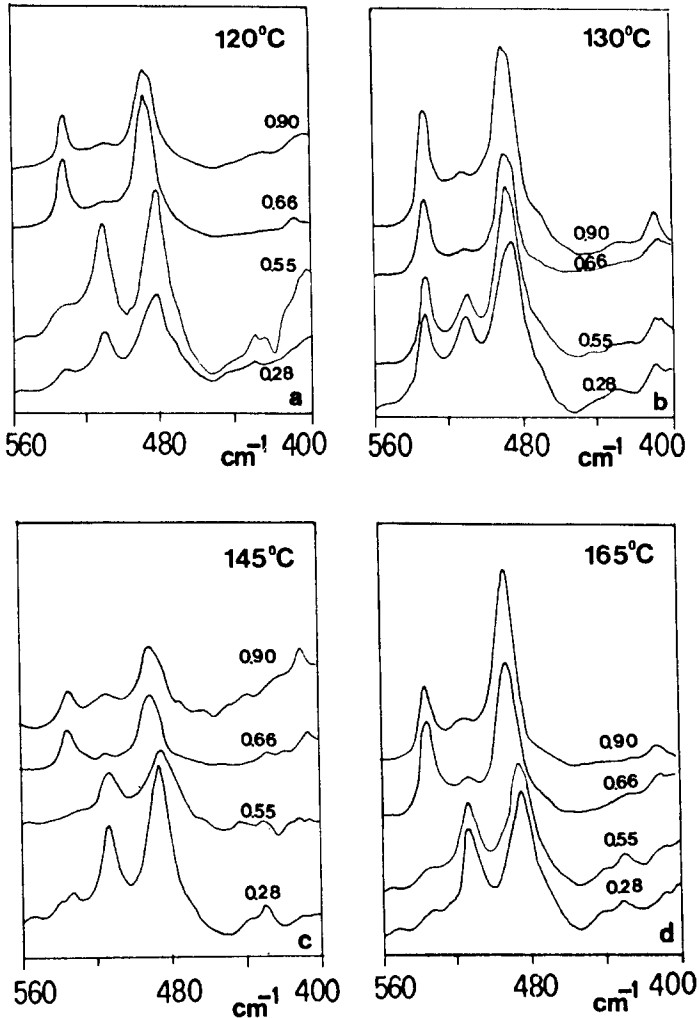
Fig.4   FT-IR spectra of PVDF films with different intrinsic viscosity
        annealed at: 120°C (a), 130°C (b), 145°C (c) and 165°C (d).

Conclusions

FT-IR examination of a series of PVDF samples with molecular weights
ranging from about 45,000 to 260,000, prepared under the same
polymerization conditions and with the same amount of reverse
addition,indicates the influence of the molecular weight in determining
the predominance of one form, with respect to the others, in samples
obtained by casting from solutions or during annealing. It is worth while
emphasizing that at the annealing temperature of 165°C, form II
prevails for higher molecular weights, while form III is obtained for low
molecular weights.These data may be useful for the preparation of a

single crystalline form for basic research or industrial application.

Aknowledgment

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