

Isomorphism Phenomena in Systems Containing Fluorinated Polymers and in New Fluorinated Copolymers

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Synopsis

High molecular weight vinyl fluoride (VF)-vinylidene fluoride (VF₂) and vinyl fluoride (VF)-tetrafluoroethylene (TFE) copolymers in a wide range of compositions have been synthesized at low pressure at 25°C. with the aid of a catalytic system consisting of triisobutyl boron activated with molecular oxygen. With the same catalytic system, highly crystalline homopolymers of VF and VF₂, melting above the usually reported temperatures, have been obtained. The x-ray and thermal analyses of crystalline molecular mixtures of PVF and PVF₂, as well as of VF-VF₂ copolymers, have shown that in both cases the monomeric units of the two types may be present in the same crystallites, giving rise to a phenomenon very similar to the isomorphism in the case of low molecular weight substances; an analogous phenomenon was already described by some of us¹ for other polymeric systems. In the actual case we have observed the isomorphism between the VF and VF₂ monomeric units in all the range of compositions, both for the homopolymer mixtures and for the copolymers. The VF-TFE copolymer samples, in the range of compositions examined (0-75% in TFE) show a crystal structure essentially similar to that of PVF. Due to the fact that the crystal structure of PVF is not strictly analogous to that of PVFE, in the compositions containing 75-100% TFE units a phenomenon of isodimorphism, or isopolymorphism, probably takes place. Over a wide range of compositions of the monomeric reactant mixture, a marked tendency for formation of alternating (. . . ABAB . . .) sequences within the copolymer chains has been observed.

Introduction

In previous papers^{1,2} we classified isomorphism phenomena in the macromolecular field into two different types.

(a) In chain isomorphism phenomena, from mixtures of chemically different polymers, products are obtained having a defined crystalline structure, with values of the unit cell constants intermediate between those of the two polymers. We have thus a true molecular isomorphism (mutual substitution of different molecules in the crystalline lattice without any sharp structural variation). In these cases it is possible to separate the macromolecules of the two types by physical methods.

(b) Isomorphism phenomena of monomeric units of different types con-

tained within the same macromolecules as a result of a copolymerization process differ substantially from the isomorphism phenomena (a) because the isomorphous units are chemically bound to each other and therefore cannot be separated by physical methods. In these cases, a mixed crystallization of the two types of monomeric units occurs; this phenomenon is analogous in some respects to the well known isomorphism among low molecular weight substances, if we substitute the concept of the monomeric unit for the usual concept of a molecular unit. This phenomenon can be considered as a particular case of isomorphism, also because the effects on certain physical properties of the copolymers (continuous variation of the properties with composition) show some analogies to those pertaining to the solid solutions of type (a).

Studies^{1,2} carried out in our Institute on isomorphism phenomena in macromolecular systems have already demonstrated a chain isomorphism phenomenon in the crystalline molecular mixtures of isotactic polystyrene and of a styrene-*p*-methylstyrene copolymer. Moreover isomorphism and isodimorphism phenomena of monomeric units have been observed in the case of different crystalline copolymers obtained from styrene and substituted styrenes. In particular, isomorphism has been observed in styrene-*o*-fluorostyrene copolymers, and isodimorphism in the styrene-*p*-fluorostyrene and styrene-*p*-methylstyrene copolymers.

In the case of low molecular weight substances, isomorphism occurs when the dimensions of the isomorphous molecules are slightly different; by analogy we have confined our attention to systems in which various monomeric units differed due to the substitution of some atoms by others having a slightly different van der Waals' radius. Other factors playing an important role in the formation of mixed crystals are the similarity between the crystal structures of the pure substances, and in particular, in the case of polymers, the analogy between the conformations of the macromolecules in the crystal line state.¹⁻³ Therefore we confined our attention to systems consisting of macromolecules in which hydrogen atoms in different positions have been replaced by fluorine atoms. We wish to remark here that the van der Waals' radius of fluorine (~ 1.35 A.) is slightly different from that of hydrogen (~ 1.25 A.), and that the C—H and C—F bond distances are not very different (~ 1.10 and ~ 1.35 A., respectively).⁴

In order to satisfy the conditions of similarity in chain and crystal structure, we have considered in particular the polymeric systems consisting of vinyl fluoride (VF), vinylidene fluoride (VF₂), and tetrafluoroethylene (TFE) units. We shall briefly describe the crystal structures of the three corresponding homopolymers, pointing out the structural analogies that led us to make this choice.

Chain and Crystal Structure of Poly(vinyl Fluoride) (PVF), Poly(vinylidene Fluoride) (PVF₂) and Polytetrafluoroethylene (PTFE)

The crystal structure of PVF⁵ was described⁵ as resulting from a packing of chains having a planar zigzag conformation, so that the axes of the mac-

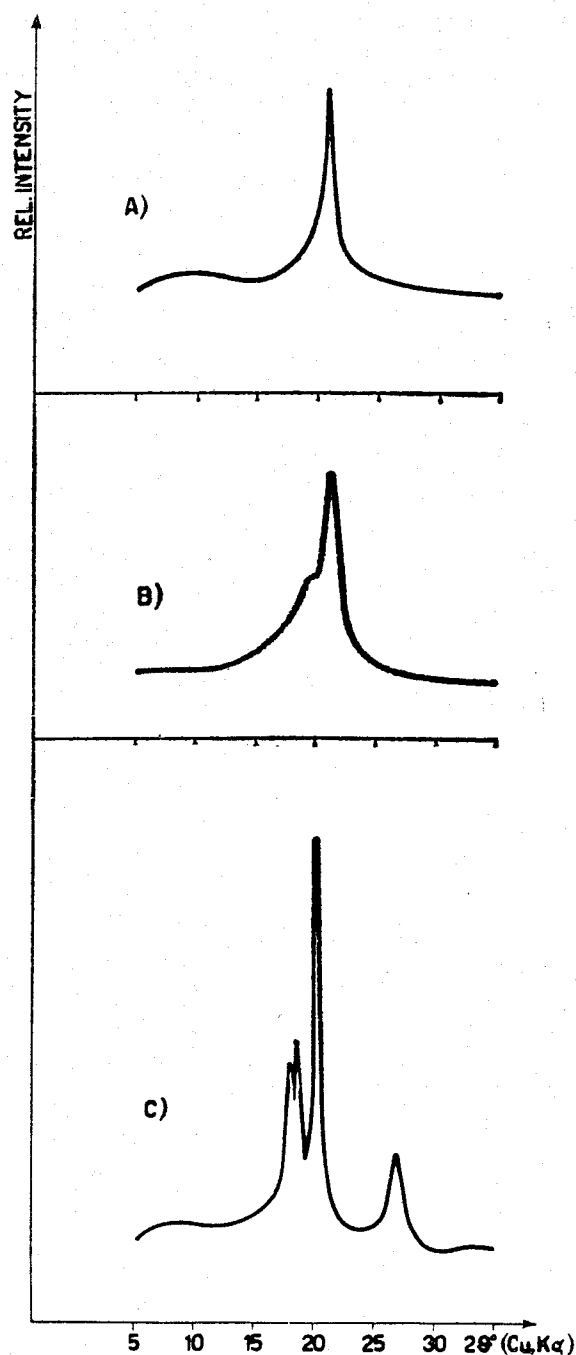


Fig. 1. Powder x-ray diffraction spectra ($\text{CuK}\alpha$) obtained with a Geiger-tube spectrogoniometer: (A) PVF; (B) PVF_2 , modification I; (C) PVF_2 , with simultaneous presence of modifications II and III and perhaps I.

romolecules at van der Waals contact are all 4.95 Å. apart. The chain repeat length is 2.52 Å. and corresponds to only one monomeric unit; the configuration of the macromolecules was substantially atactic in all the samples examined by us.

Polymorphism of crystalline PVF_2 has been recently observed by Makarevich and also by us.⁶ According to our results, this polymer may have at least three modifications (see Fig. 1); one of them (modification I) is characterized by a planar zigzag chain conformation and by a crystal structure quite similar to that reported for PVF, except for a slight in-

crease in the distances between the chain axes of adjacent molecules (5.04 Å.) and in the chain repeat (2.57 Å.). Another modification (modification II) is characterized by a chain repeat of 4.66 Å., corresponding to two monomeric units. With regard to modification III, the data at our disposal do not allow its structural characterization; a more or less complete transition from the planar form, which can be obtained for instance by stretching of molded sheets or extruded filaments at room temperature, to a mixture of modifications II and III may be reached by melting and subsequent cooling of the sample.

Crystalline PTFE seems to exhibit three different modifications; one (modification I) is stable below 20°C., another one (modification II) between 20 and 30°C., and the third one (modification III) is stable above 30°C. All the modifications correspond to a pseudo-hexagonal packing of the chains; quoted values of the distances among the axes of the adjacent macromolecules are 5.59 Å. (modification I) and 5.66 Å. (modification II). The chain conformation is described as a helix containing 6.5 monomeric units in 6 pitches for modification I and 7.5 units in 7 pitches for modification II.⁷ In the transition I → II, therefore, a certain untwisting of the macromolecule occurs, which seems to increase further in the transition II → III.⁷ The monomeric unit repeat along the chain axis is of about 2.59 Å. in all cases.

It is therefore possible to detect certain structural analogies among the polymers mentioned above. In particular, modification I of PVF₂ has a structure quite analogous to that of crystalline PVF. Moreover, the chain conformations of PTFE in its different modifications, in spite of the chain twisting, are near to the planar zigzag conformation, and they probably tend to attain it at increasing temperature.⁷ Moreover, the molecular packing is characterized, in all these cases, by a pseudo-hexagonal arrangement of the macromolecules.

All these factors have induced us to assume the possibility of obtaining mixed crystals both in suitable solid mixtures containing macromolecules of the above types, and in copolymers in which the corresponding monomeric units are present. In particular, we will describe the preparation and properties of the following systems: (1) crystalline molecular mixtures of PVF and PVF₂ homopolymers of various compositions; (2) crystalline VF-VF₂ and VF-TFE copolymers of various compositions.

Synthesis of the Polymers and Copolymers

Systematic investigations of the copolymerization of VF with other vinyl monomers have not been reported in the literature; this is probably due to the considerable difficulties in obtaining PVF having a sufficiently high degree of polymerization. In fact, as it is known, for this purpose it is necessary to operate under very drastic polymerization conditions, with monomer pressure of several hundreds of atmospheres.⁸

In order to synthesize the homopolymers and the VF-VF₂ and VF-TFE copolymers, we used catalytic systems consisting of boron trialkyl com-

pounds activated by weighed proportions of molecular oxygen; these systems have proved to be particularly active at low temperatures. The use of initiators of this type has been previously described for the polymerization of other vinyl monomers.⁹ These catalytic systems, when adapted to the polymerization of VF, enabled us to obtain high molecular weight polymers even with a liquid monomer at room temperature and therefore under slight autogenous pressures. PVF thus obtained is highly crystalline and its melting temperature, corresponding to complete disappearance of birefringence, is above 230°C. This temperature is considerably higher than the melting temperature (195–200°C.) of PVF obtained by the usual polymerization processes at high pressures.^{10,11}

Under the same conditions, we have ascertained that also VF₂ and TFE are polymerized to high polymers showing a high degree of crystallinity. PVF₂ obtained in such a way has a melting temperature higher by about

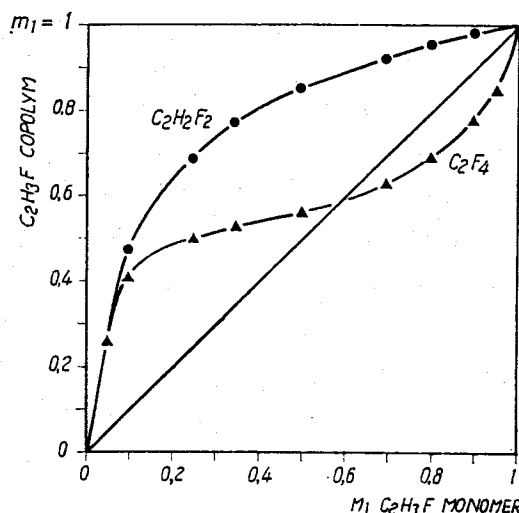


Fig. 2. Copolymerization diagram of VF-TFE and VF-VF₂ systems.

10°C. than that usually reported for such a polymer.¹² By this polymerization method we prepared copolymers with various compositions from mixtures of VF both with VF₂ and with TFE.

In Figure 2 are shown the molar compositions of the monomeric reactant mixtures versus the molar composition of the copolymers for the two systems.

The reactivity ratios r_1 and r_2 , determined by the usual methods for the two copolymerization processes are: $r_{1(\text{CH}_2=\text{CHF})} = 5.5 \pm 0.5$, $r_{2(\text{CH}_2=\text{CF}_2)} = 0.17 \pm 0.03$; and $r_{1(\text{CH}_2=\text{CHF})} = 0.27 \pm 0.03$, $r_{2(\text{CF}_2=\text{CF}_2)} = 0.05 \pm 0.02$.

If we consider for the two systems the product $r_1 r_2$ and the shape of the two curves of Figure 2, it is clear that the copolymerization of VF with VF₂ under these conditions follows a behavior very close to ideal behavior ($r_1 r_2 = 1$); consequently it can be assumed that in these copolymers the two different units are arranged along the macromolecules virtually at random. In the copolymerization of VF with TFE, on the other hand, we observe behavior typical of two monomers which tend to give rise to an alternating

copolymer. Therefore the resulting system will have constant composition, near to 50:50, over a wide composition range of the monomer mixture.

X-Ray and Thermal Analyses of Solid Mixtures of PVF-PVF₂ Homopolymers

The x-ray analysis of powder samples with the use of a Geiger-tube spectrogoniometer, revealed the presence of high crystallinity (of the order of 70% at least) in all the examined samples; their compositions are reported in Table I.

TABLE I
Weight Compositions of PVF-PVF₂ Mixtures

Sample no.	PVF, wt.-%	PVF ₂ , wt.-%
1	80	20
2	60	40
3	40	60
4	25	75
5	10	90
6	5	95

Moreover, in the d range between 5 and 4 Å., only one crystalline peak, with a Bragg distance ranging from 4.31 to 4.39 Å., was observed (see Fig. 1) in all the samples, even in those with the highest content of PVF₂ (95%), either at room or at higher temperatures. This peak is characteristic of the planar zigzag crystalline modification of PVF₂ (modification I), which is very similar to the crystal structure of PVF.

We wish to point out, incidentally, that the extreme values of the Bragg distances d corresponding to the peak under consideration (4.31 and 4.39 Å.), are very slightly different. As a consequence, the actual value of the above distance for a given sample cannot *a priori* be taken as a parameter associated with its composition, both in the case of macromolecular mixtures and in the case of copolymers.

The results reported above cannot be explained other than by assuming the formation of crystallites in which both types of macromolecules are present. In fact, let us suppose that a segregation of the two types of macromolecules in different crystals takes place, even to a limited extent. In such a case, in contrast with our experience, we should certainly observe the presence of modifications II and III of PVF₂, especially if the samples undergo melting and subsequent cooling. On the other hand, the high degree of crystallinity always observed is well explained on the basis of complete chain isomorphism between the two polymers.

The melting temperatures of the systems reported in Table I, corresponding to complete disappearance of the crystalline peaks, led to the values reported in Fig. 3a. The melting temperature reported for pure PVF₂ corresponds to that of modification I. All the temperatures were deter-

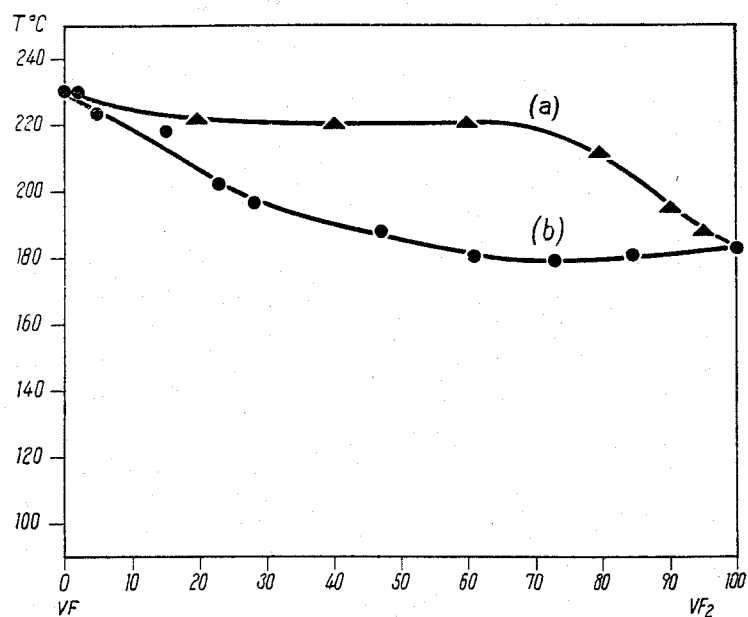


Fig. 3. Melting temperatures of (a) PVF₂-PVF mixtures and of (b) VF₂-VF copolymers.

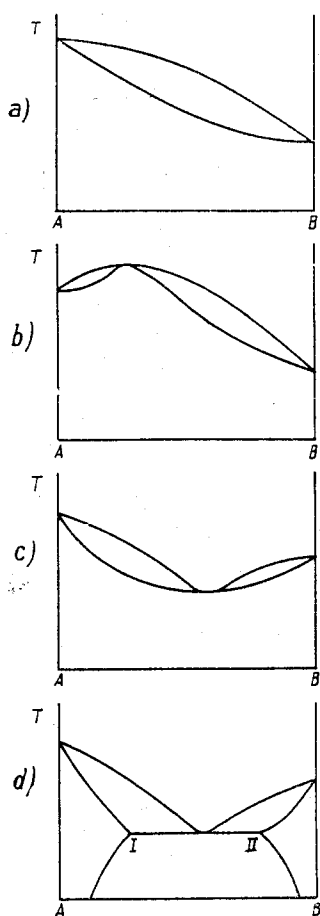


Fig. 4. Phase diagrams of binary systems showing (a, b, c) isomorphism in the whole range of compositions and (d) of systems showing isomorphism only for limited ranges of compositions (isodimorphism).

mined with a very slow heating and cooling rate (-1°C./min. near melting), in order to approach the thermodynamic equilibrium conditions as much as possible. As it can be seen, the resulting diagram is substantially analogous to that to be expected in the case of a binary system showing isomorphism in the solid state within the whole range of compositions (see Fig. 4a), when no maximum or minimum point occurs for the melting temperatures.

X-Ray and Thermal Analysis of VF-VF₂ Copolymers

The VF-VF₂ copolymer samples examined by us correspond to the compositions reported in Table II. The x-ray examination, with a Geiger-tube

TABLE II
Weight Compositions of VF-VF₂ Copolymers

Sample no.	VF, wt.-%	VF ₂ , wt.-%
1	98.0	2.0
2	95.3	4.7
3	85.2	14.8
4	72.0	28.0
5	53.0	47.0
6	39.0	61.0
7	27.0	73.0
8	16.0	84.0

spectrogoniometer, was performed on powder samples as obtained from the polymerization process. Oriented fibers obtained by extrusion from the melt and subsequently stretched, were then examined by a cylindrical camera. The presence of only one crystalline modification, characterized by a very intense peak (Fig. 5) with a Bragg distance ranging from 4.31 Å, in the case of pure PVF (Fig. 1A) to 4.39 Å in the case of pure PVF₂ (Fig. 1B) was observed. As in the case of the homopolymer mixtures, even after thermal treatment, no evidence was observed of any crystalline modification analogous to modifications II and III of PVF₂ (Fig. 1C).

The fact that the degree of crystallinity of all the samples under examination was always very high (of the order of 70–80%) led us to accept the conclusion that an isomorphous substitution phenomenon of the two comonomers occurs in all composition ranges. If the units of both types were not present in the same crystallites, the high degree of crystallinity of these copolymers could not be explained. This is even more so considering that the behavior of the copolymerization of the two monomers, discussed in the previous section, agrees with the hypothesis of a "random" distribution of the VF and VF₂ monomer units along the chain. In this case too, modifications II and III of PVF₂ are always absent even in samples with a high VF₂ content; this demonstrates that a strong stabilization effect on the planar zigzag chain conformation is induced by the VF units, even in a small concentration.

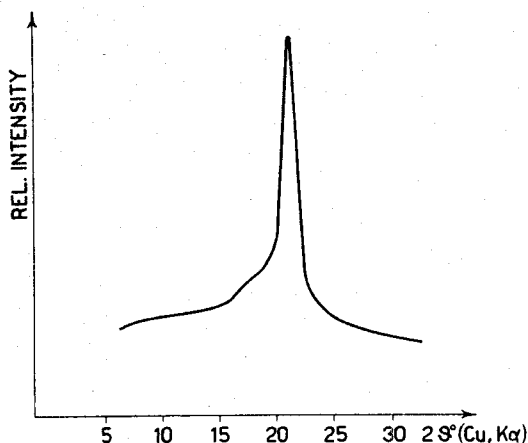


Fig. 5. Powder x-ray diffraction spectrum ($\text{CuK}\alpha$) obtained with a Geiger-tube spectrogoniometer from a VF-VF₂ copolymer sample (weight composition 1:1).

The diagram of the melting temperatures of the samples, corresponding to complete disappearance of the crystalline peaks, is shown in Figure 3*b* (heating and cooling rate -1°C./min. near melting). It can be observed that for a composition ranging from 60 to 80% of vinylidene units, a minimum for the melting temperatures seems to be present. If this evidence is true, we should be in presence of a phenomenon analogous to that occurring in some binary systems showing isomorphism over the whole composition range, characterized by an intermediate minimum of melting temperatures (Fig. 4*c*). Any possibility that such a minimum might correspond to an eutectoid point (Fig. 4*d*) that is characterized by the presence of two different solid solutions having a different crystalline structure (isodimorphism), seems to be excluded due to the absolute identity of the crystalline structure over the entire composition range.

It is interesting to compare the behavior of the melting temperatures reported in Figure 3 in the two cases of homopolymer mixtures (curve *a*) and of copolymers (curve *b*). The melting temperatures of the mixtures are always higher than those for copolymers of corresponding composition; this seems to open an interesting field of thermodynamic studies in the binary systems of this type.

X-Ray and Thermal Analysis of the VF-TFE Copolymers

The VF-TFE copolymers, whose compositions are reported in Table III, show the presence of a certain degree of crystallinity. Fibers obtained both by extrusion from the melt and subsequent stretching, and by stretching of molded sheets, show a good orientation of the crystallites.

The equatorial reflections of the fiber spectra of all the samples examined, may be indexed on the basis of hexagonal unit cells. Their dimensions increase with increasing TFE content in the copolymer. In Figure 6, we show as examples the powder spectra obtained with a Geiger-tube spectrogoniometer from a PVF sample, from a copolymer sample in which the two comonomers are in 1:1 ratio, and from a sample of PTFE. The intense reflection observed for all the three polymers has hexagonal indexes (10 $\bar{1}$ 0).

TABLE III
Molar and Weight Compositions of VF-TFE Copolymers

Sample no.	TFE, mole-%	TFE, wt.-% weight composition
1	14.5	28.5
2	22.0	38.0
3	31.0	49.4
4	37.0	56.1
5	44.0	63.1
6	47.0	65.7
7	50.0	68.5
8	59.0	75.8
9	74.0	86.1
10	77.0	87.9
11	78.0	88.5

Starting from PVF, the equatorial hexagonal constant measured for the various copolymers, at least in the range of compositions examined, appears to increase about linearly with the TFE content in the copolymer. Figure 7 reports the values of the equatorial hexagonal constants against the molar

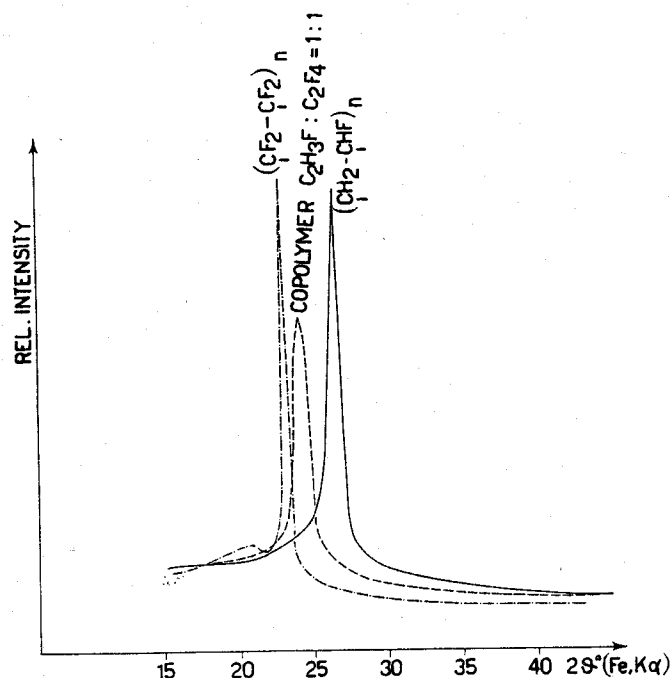


Fig. 6. Powder x-ray diffraction spectra ($\text{FeK}\alpha$) obtained with a Geiger-tube spectrogoniometer from samples of PVF, PTFE, and of a VF-TFE copolymer.

composition of the samples. For copolymer samples having a TFE molar content higher than 75%, the linearity dependence of the equatorial constant on the molar composition cannot be further maintained; however, we could not examine any copolymer sample in this range of compositions, due to great experimental difficulties in the chemical synthesis.

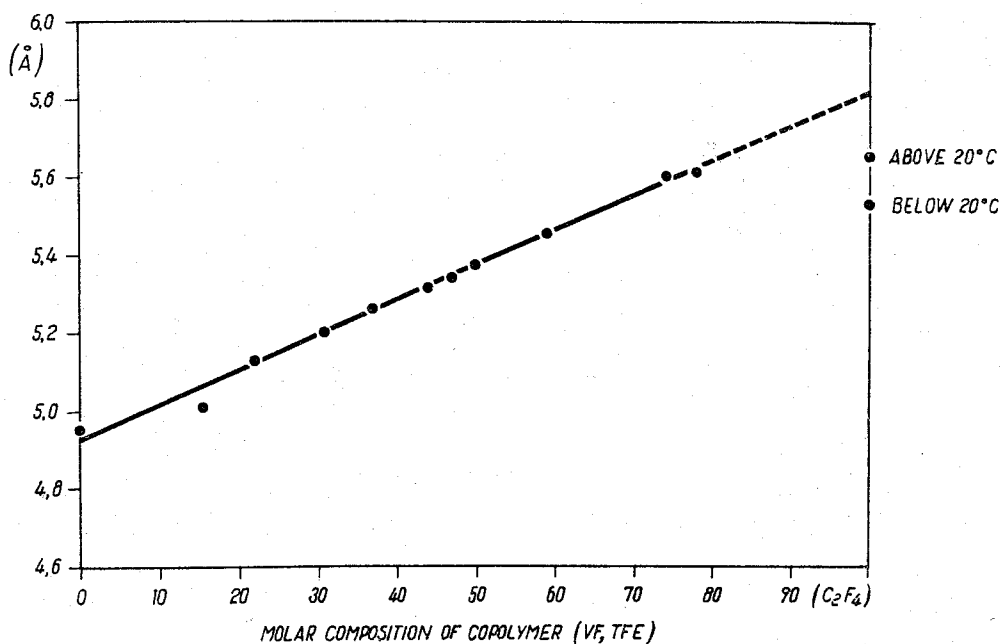


Fig. 7. Plot of the equatorial hexagonal constants of crystalline VF-TFE copolymers against molar composition.

The nonequatorial reflections appearing in the x-ray fiber spectra are largely spread along the layer lines. This effect is certainly connected with a statistical distribution of the two types of monomer units along the chains.

For copolymers with a low TFE content, a chain repeat of about 2.54 Å is measured. From this value and from examination of spectra of the tilted fiber, we have deduced that the main chain has still a planar zigzag conformation, as in the case of PVF. For copolymers having a molar composition ranging from 20 to 60% TFE, new layers, very weak in intensity, appear on the fiber spectra (Fig. 8), and correspond to a chain repeat about twice the above value (5.10 Å). The appearance of these new layers, beside proving the actual presence along the macromolecules of both kinds of monomeric units, must be connected with a high proportion of alternating successions of VF and TFE units. This phenomenon shows some analogy with the formation of superstructures in solid solutions of low molecular weight substances after particular thermal treatments. Apparently, a pseudoregularity in the monomer unit distribution in our case, however, can be due only to the polymerization process. The tilted-fiber spectra of these copolymers show two sharp equatorial reflections corresponding to interplanar distances d of 2.55 and 1.27 Å. These values are in a 1:2 ratio and show that the macromolecule again assumes a planar zigzag conformation. The reflection with $d = 2.55$ Å is due to the difference in scattering power between the CH_2 and the CHF units; no contribution to this reflection is attributable to the $\text{—CF}_2\text{—CF}_2\text{—}$ monomer units. Moreover, a nonzero value of the corresponding intensity is necessarily connected with a constant orientation of the $\text{—CH}_2\text{—CHF—}$ units with respect to the chain axis, at least for sufficiently long sequences inside the macromolecules.

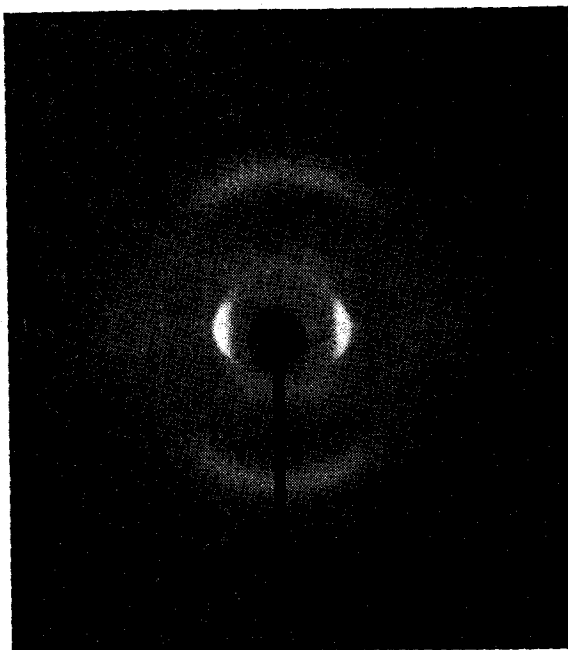


Fig. 8. X-ray fiber spectrum of a VF-TFE copolymer (molar composition 1:1).

Let us consider now the copolymers having a TFE molar content ranging from 70 to 75%; their equatorial constant (Fig. 7) assumes values intermediate between those found for PTFE in the stable modifications below and above 20°C. The oriented fiber x-ray spectra show only the presence of layers corresponding to a chain repeat of 2.55 Å., and a sharp equatorial reflection is observed on the tilted-fiber spectra with $d = 1.27$ Å. It seems reasonable to attribute a planar conformation of the main chain to these copolymers also. The proportion of alternate successions of monomeric

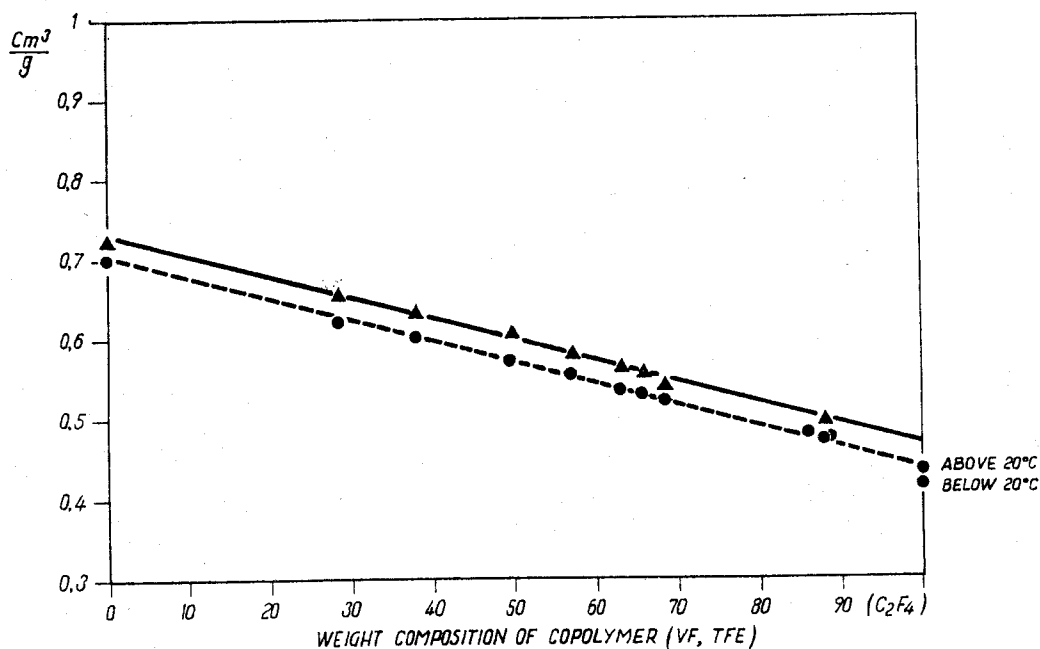


Fig. 9. Experimental and calculated specific volume of crystalline VF-TFE copolymers vs. the weight composition.

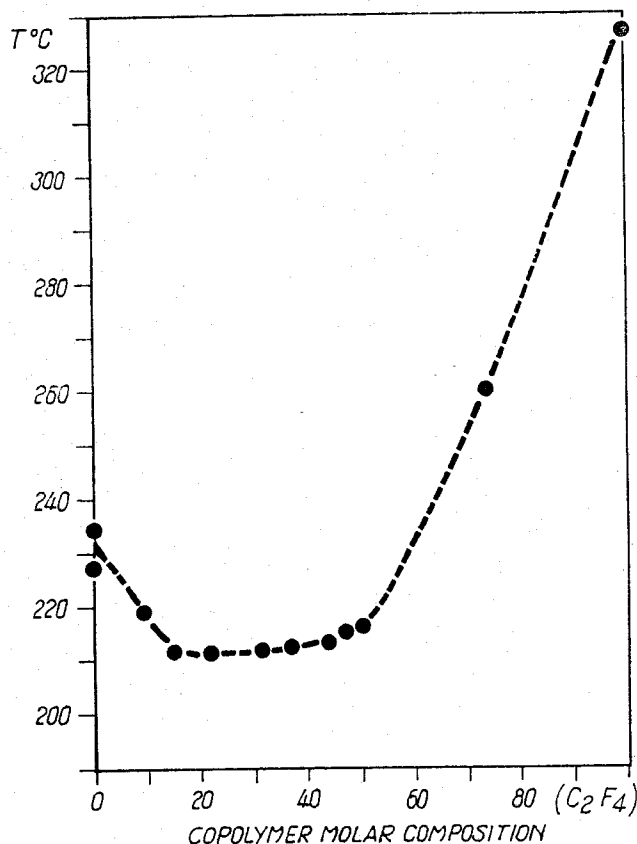


Fig. 10. Melting temperatures of crystalline VF-TFE copolymers as a function of the molar composition.

units of the two types in these cases seems to be sharply reduced, so that it can no longer be detected.

To prove further the continuity of crystalline structure over the entire range of copolymer compositions examined, we made a comparison between the dependence of the specific volumes calculated from the x-ray data and those found experimentally from the weight composition. As seen in Figure 9, the agreement between calculated and experimental data is quite satisfactory. The diagram shows a linear dependence of both the calculated and the experimental specific volumes over the entire composition range examined.

The melting temperatures of the VF-TFE copolymers of various compositions, determined by a polarizing microscope, are reported in Figure 10. Over a wide range of molar compositions, ranging from 15 to 50% in TFE, a nearly flat variation of the melting temperatures is observed; these temperatures are considerably lower than those of both homopolymers. It is interesting to observe that such a composition range corresponds approximately to that in which the fiber spectra indicate the presence of alternate arrangements of the two comonomers.

Experimental

Copolymerizations of both monomer pairs (VF-VF₂ and VF-TFE) were carried out in a 50 cm.³ stainless steel autoclave into which, with ex-

clusion of air, 2 cm.³ of ethyl acetate containing 0.2×10^{-3} g.-mole of triisobutyl boron was introduced. After cooling the container to -80°C . under vacuum, 2.0 cm.³ of O₂ was introduced and then 0.2 g.-mole of the monomeric mixture with the wanted composition was condensed. The reaction was carried out by keeping the autoclave, with rocking, in a thermostatted bath at 25°C . until the desired degree of conversion (usually 3–6%) was reached. At the end of the reaction, the residual monomeric mixture was removed, and the copolymer was thoroughly washed with boiling methanol and dried to constant weight. Its composition was determined by elementary analysis.

The intrinsic viscosity of all the copolymers was always in the range of 0.5–2 (100 cm.³/g.). Measurements were carried out in dimethylformamide solution at 110°C ., even the copolymers containing a high content of TFE being sufficiently soluble in that solvent. Homogeneous mixtures of the PVF and PVF₂ homopolymers were obtained by dissolving 1.0 g. of a polymer mixture of known composition in about 300 cm.³ of dimethylformamide at about 120 – 150°C . The solution was hot-stirred for about 2 hr., and was then hot-filtered on a glass porous baffle. The solution was then slowly poured with stirring into 1000 cm.³ of a methanol–water mixture (50:50, v/v). The precipitated polymer was filtered, washed with methanol, and dried to constant weight. In all the runs, the recovery of the polymers was practically quantitative.

The densities of the VF–TFE copolymer samples were determined by flotation of molded sheets annealed at about 150°C . for 4 hr., mixtures of dioxane and ethylene bromide being used flotation liquids.

Conclusions

The following solid crystalline systems of various compositions have been examined: molecular mixtures of PVF and PVF₂; VF–VF₂ copolymers; VF–TFE copolymers.

The x-ray and thermal examination of the first two systems have indicated the presence of vinyl and vinylidene units in the same crystallites; this phenomenon, observed over the whole range of compositions, is quite analogous to that of complete isomorphism between low molecular weight substances. With the exception of the already known isomorphism between monomeric units only differing by isotopic substitution (e.g., propylene and deuteropropylene), this is the first example fully described of isomorphism over an entire range of compositions, existing simultaneously both between the macromolecules of two different polymers and between the monomeric units in the corresponding copolymers. The two types of systems are quite different with regard to their melting temperatures (see Fig. 3); the copolymer melting temperatures are systematically lower than those corresponding to the macromolecular mixtures of equal overall composition. Complete isomorphism is possible by the presence of a crystalline structure of PVF₂ (modification I) which is quite analogous to the crystal structure of PVF: both are characterized by a planar zigzag

macromolecular conformation, and the unit cell of PVF_2 is only slightly broadened (1–2% in linear dimensions) with respect to that of PVF.

The experimental data reported in the present paper for VF–TFE copolymers are probably to be interpreted on the basis of an isodimorphism, or isopolymorphism, between the monomeric units of the two types. In fact, in this case, complete isomorphism with a single crystal structure in the whole composition range is impossible because no sufficiently close analogy exists between the crystal structures of PVF and PTFE.

In the field of compositions examined by us (0–75% TFE), only one crystalline phase is observed; this is substantially analogous to that of PVF, except for the continuous variation in the equatorial size of the unit cell and the presence of relatively long sequences, in which the VF and TFE units alternate regularly (15 + 50% of TFE). In the range of compositions not investigated by us (75–100% TFE), there must occur one or possibly more different crystalline structures; in fact, for compositions approaching 100% in TFE, crystalline modifications of PTFE must arise.

Finally it must be remarked that the introductions of VF units in the PTFE chain, even in low amounts, leads to a stabilization of the planar zigzag conformation of the chains, with some analogy to the untwisting effect which is produced by an increase in temperature on the PTFE macromolecules.⁷

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Résumé

Des copolymères de poids moléculaire élevé de fluorure de vinyle (VF)/fluorure de vinylidène (VF_2) et de fluorure de vinyle (VF)/tétrafluoroéthylène (TFE) ont été synthétisés sur une vaste échelle de composition sous faible pression à la température de 25°C. à l'aide d'un système catalytique qui consiste en du triisobutyle-bore activé à l'oxygène moléculaire. On a obtenu au moyen de ce même système catalytique des homopolymères fortement cristallins de VF et VF_2 qui fondent au-dessus des températures ordinairement signalées. Les analyses thermiques et analyses par rayons-X, aussi

bien des mélanges moléculaires cristallins de PVF et PVF₂, que des copolymères VF/VF₂, démontrent que dans les deux cas on peut trouver des unités monomériques des deux types, dans les mêmes cristallites, ce qui donne lieu à un phénomène très semblable à l'isomorphisme dans le cas des substances de faible poids moléculaire; un phénomène analogue a déjà été décrit par certains d'entre nous pour d'autres systèmes polymériques (1). Dans le cas présent nous avons observé un phénomène d'isomorphisme entre les unités monomériques de VF et VF₂ dans toute la gamme des compositions, aussi bien pour les mélanges d'homopolymères que pour les copolymères. Les échantillons du copolymère VF/TFE, dans le domaine des compositions examinées par nous (0-75% en TFE) montrent une structure cristalline essentiellement semblable à celle du PVF. Du fait que la structure cristalline de PVF n'est pas strictement analogue à celle de PTFE, dans le domaine de compositions de 75 à 100% en unités de TFE, un phénomène d'isodimorphisme ou d'isopolymorphisme a probablement lieu. Dans un large domaine de compositions du mélange monomérique dans le milieu de réactions, on a observé une forte tendance à la formation de séquences alternantes (ABAB) au sein des chaînes polymériques.

Zusammenfassung

Hochmolekulare Vinylfluorid (VF)/Vinylidenfluorid-(VF₂) und Vinylfluorid (VF)/Tetrafluoräthylen-(TFE) copolymere wurden in einem weiten Zusammensetzungsbereich bei niedrigem Druck bei 25°C. mit Hilfe von Katalysatorsystemen aus mit molekularem Sauerstoff aktiviertem Triisobutylbor synthetisiert. Mit dem gleichen Katalysatorsystem wurden VF- und VF₂-Homopolymere mit höheren als den üblichen Schmelzpunkten erhalten. Die Röntgen- und die thermische Analyse kristalliner molekularer Mischungen von PVF- und PVF₂ sowie von VF/VF₂-Copolymeren zeigten, dass in beiden Fällen die Monomerbausteine der beiden Typen im selben Kristall vorhanden sein können, was zu einem, der Isomorphie im Falle niedermolekularer Substanzen ähnlichen Phänomen führen kann; ein analoges Phänomen wurde von den Autoren schon für andere Polymersysteme beschrieben. Tatsächlich wurde das Isomorphiephänomen zwischen VF- und VF₂-Monomerbausteinen im gesamten Zusammensetzungsbereich sowohl für die Homopolymere als auch für die Copolymeren beobachtet. Die VF/TFE-Copolymerproben zeigen im untersuchten Zusammensetzungsbereich (0-75% TFE) eine im wesentlichen derjenigen des PVF ähnliche Kristallstruktur. Wegen der nicht strengen Analogie der Kristallstruktur von PVF zu derjenigen von PTFE tritt wahrscheinlich im Zusammensetzungsbereich von 75-100% TFE ein Isodimorphie- oder Isopolymorphiephänomen auf. Für einen grossen Zusammensetzungsbereich der Monomerenmischung wurde eine starke Tendenz zur Bildung alternierender (...ABAB...) Sequenzen innerhalb der Copolymerketten beobachtet.

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