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COPOLYMERIZATION OF ETHYLENE AND CHLOROTRIFLUOROETHYLENE BY TRIALKYLBORON CATALYSTS—II.

PHYSICO-CHEMICAL CHARACTERIZATION OF THE COPOLYMERS

C. GARBUGLIO, M. RAGAZZINI, O. PILATI, D. CARCANO and GB. CEVIDALLI

Montecatini Edison S.p.A., Centro Ricerche, Bollate (Milano), Italy

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Abstract—Melting point, crystallinity and alternation of the units in the chain of ethylene–chlorotrifluoroethylene copolymers have been investigated in relation with the copolymer compositions and the polymerization temperature. Determinations have been carried out by i.r., X-ray and optical microscopy methods. A new repeating unit is formed by regular alternation of CH_2—CH_2 and CF_2—CFCl units along the polymer chain: it is able to crystallize according to a new crystal structure. Melting point, entropy and enthalpy of fusion of the completely alternating copolymers have been determined. The polymerization temperature affects the stereochemical regularity of the polymer chain.

INTRODUCTION

IN PREVIOUS work[1] on the copolymerization of ethylene and chlorotrifluoroethylene we pointed out, on the basis of reactivity ratios, a marked tendency toward regular alternation of the comonomers particularly at low temperatures. The copolymers were found to be crystalline. In this work, the alternation of units in the chain, the crystallinity and the melting point of the same copolymers have been related to the polymerization temperature and copolymer compositions. The investigation has been carried out by i.r., X-ray and optical microscopy analysis. The results indicate that the regular alternation of CH_2—CH_2 and CF_2—CFCl units leads to a new repeating unit which has definite thermodynamic characteristics and is able to crystallize in a particular crystal structure.

EXPERIMENTAL

(*a*) *Melting temperature*

The melting temperature was assumed as the temperature of disappearance of the last traces of birefringence. A Leitz–Wetzlar hot-stage polarizing microscope with 100× magnification was used. The samples, in the form of thin films, were annealed at temperatures close to the melting temperatures, with the aim of achieving the maximum crystallinity degree and obtaining the maximum amount of the most perfect crystallites. A slow heating rate (0·5°/min) was chosen. Reproducibility of the determinations was ±1°.

(*b*) *Infra-red measurements*

High resolution spectra in the range of 2–7 μ were recorded with a model 125 Perkin–Elmer grating spectrophotometer. Thin films, prepared by compression moulding, were used: in no film was selective rotation to polarized light noted.

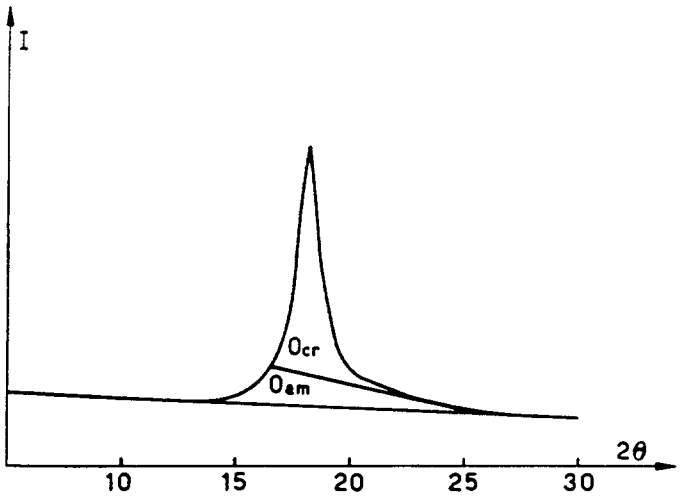

FIG. 1. Diffraction spectrum of a C_2H_4—C_2F_3Cl copolymer sample. Crystalline–amorphous separation.

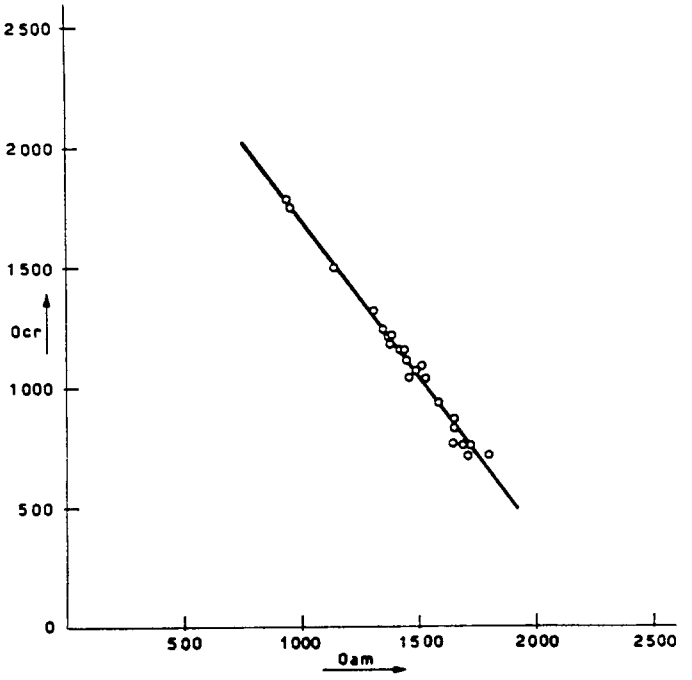

FIG. 2. Regression line of O_{cr} on O_{am} (see text).

(c) X-ray analyses

The samples, in the form of compression-moulded sheets, were examined on an X-ray diffractometer (Philips, Eindhoven) equipped with scintillation counter and pulse-height analyser. Cu–D_α radiation (Ni-filtered) was used. Fibre spectra were obtained on a flat-plate camera (Philips).

For the high-temperature measurements a "Rigaku-Denki" attachment for the diffractometer was used. Some measurements on small samples were also carried out with a Debye–Scherrer camera (57·5 mm dia.); in this case, the diffraction spectra were densitometered by a Joyce–Loebl instrument.

For the determination of degree of crystallinity, we followed a method which is analogous to that of Weidinger and Hermans for polypropylene.[2] The measurements were carried out by recording diffractograms of several samples of the same polymer, in which different crystallinity degrees were induced by different cooling and annealing treatments. The diffractograms were taken by reflection. From each diffractogram two suitable areas, related to amorphous and crystalline fractions, were selected: a regression line was calculated giving the best linear relation between them. The method does not require account to be taken of the Lorentz-polarization temperature factors and for the incoherent radiation. The spectrum of the amorphous sample was obtained by measurements above the melting point (280°). It exhibits a broad band with a maximum at about $2\theta = 16{\cdot}65°$. Crystalline-amorphous separation is illustrated in Fig. 1. The regression line is shown in Fig. 2: from the straight line the Eqn.

$$\alpha = \frac{1}{1 + 1{\cdot}31(O_{am}/O_{cr})} \tag{1}$$

is derived.

The Eqn. (1) permits calculation of the crystallinity degree α from the knowledge of the values O_{am} and O_{cr}, which are proportional to amorphous and crystalline content respectively.

RESULTS AND DISCUSSION

The curve of melting temperature for various ethylene–chlorotrifluoroethylene copolymers (synthesized at −78°) vs. composition is shown in Fig. 3. The curve shows a maximum for the 1:1 molar composition: the maximum temperature ($T_m = 264°$) is

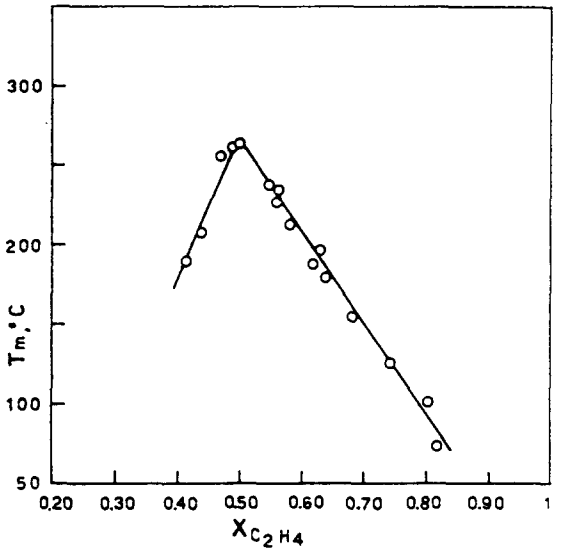

FIG. 3. Melting temperatures of C_2H_4—C_2F_3Cl copolymers, synthesized at −78°, as a function of the molar composition.

considerably higher than the melting temperatures of both linear polyethylene[3] ($T_m = 137{\cdot}5°$) and polychlorotrifluoroethylene[4] ($T_m = 220$–$225°$). To our knowledge, such a phase diagram for copolymer systems has not been reported previously. In fact, many systems have been investigated in which lowering of the melting point resulted from introducing a non-crystallizable unit in crystallizable chains.[5] Some data have been also reported recently[6–9] on the isomorphous substitution of the units in macromolecular chains: in these cases a mixed crystallization was found to occur without

maxima or minima for the melting temperatures. The "in-chain" isomorphism has been generally related to both the slightly different sizes of the different units and the similarity of the chain conformations in the crystalline state. In our case, the phase

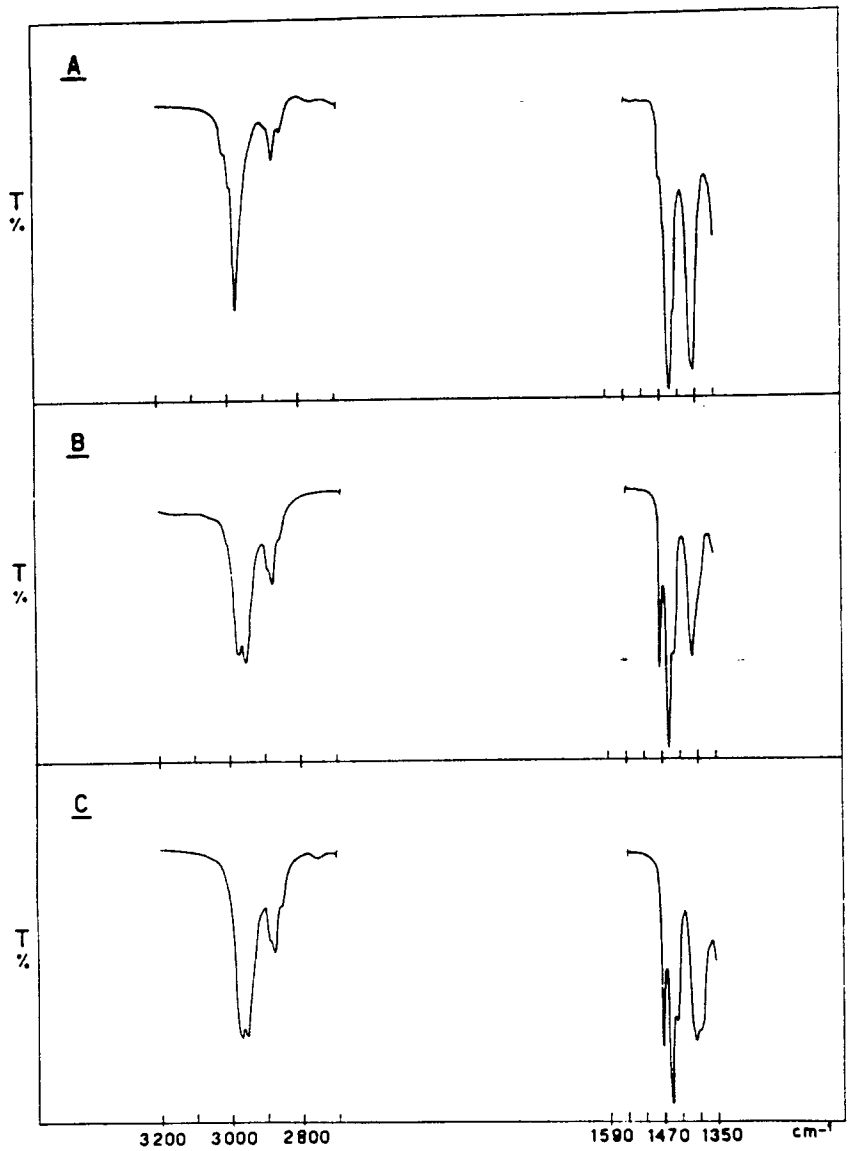

FIG. 4. Infra-red spectra of C_2H_4—C_2F_3Cl copolymers. (A) 50 per cent molar content of ethylene. (B) 55 per cent molar content of ethylene. (C) 60 per cent molar content of ethylene.

diagram is characterized by a maximum at a well-defined molar composition, as shown in Fig. 3. By analogy with phase diagrams of binary systems of low molecular weight substances, this probably indicates the presence of a crystalline compound at the maximum point of the curve. Since the corresponding ethylene–chlorotrifluoroethylene molar composition is 1:1, the polymer chain of this compound should be

built up by a regular repetition of the (CH_2—CH_2—CF_2—CFCl) unit, in such a way that a new crystalline structure may be formed with a melting point higher than those of both homopolymers (polyethylene and polychlorotrifluoroethylene). The very low values of both the reactivity ratios of the monomers are consistent with this hypothesis: in fact, for the 1:1 copolymer synthesized at $-78°$ the probability of alternation of the two different units (CH_2—CH_2 and CF_2—CFCl) is calculated to be higher than 0·99.

The existence of an exact alternation of monomeric units is also confirmed by i.r. spectroscopy in the 2–7 μ region of the spectrum. Around 3 μ the i.r. spectrum of the 1:1 copolymer made at $-78°$ exhibits only two strong peaks at 2977 ± 5 cm^{-1} and 2870 ± 5 cm^{-1} (Fig. 4). A very similar spectrum has been reported for ethylene–chlorotrifluoroethylene copolymers having a very low content of ethylene: only isolated ethylene units have been reasonably assumed in these copolymer chains.[10] The two peaks in

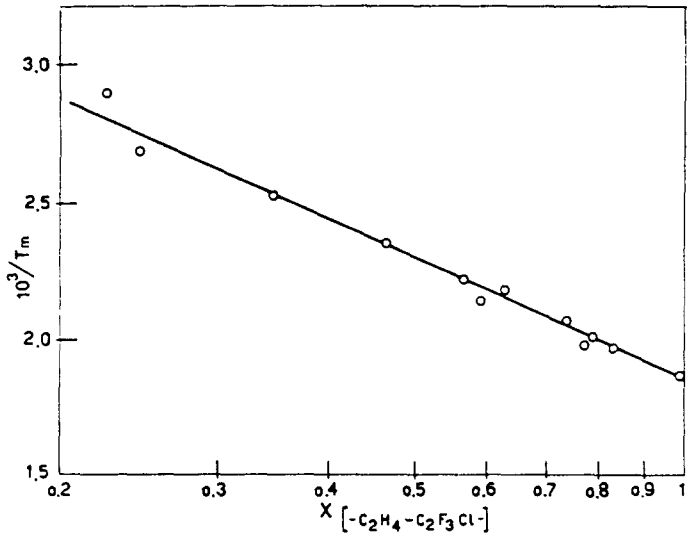

FIG. 5. Plot of $1/T_m$ against molar content of (CH_2—CH_2—CF_2—CFCl) units for ethylene–chlorotrifluoroethylene copolymers, synthesized at $-78°$.

the 3 μ region have been attributed to symmetric and asymmetric stretching vibrations of methylene groups in structures CFX—CH_2—CH_2CFX (where X = F or Cl), supposing similar interactions of CFCl and CF_2 with CH_2 groups.

In our 1:1 copolymer, only a complete alternation of the ethylene and chlorotrifluoroethylene units in the chain is consistent with such structures: however it must be pointed out that the i.r. analysis does not show the orientation of (CF_2—CFCl) units along the macromolecular chain. Quite a simple feature has been found also in the 7 μ region. The spectrum exhibits only two bands at 1449 ± 5 cm^{-1} and 1397 ± 5 cm^{-1}, which can be attributed to the scissoring and wagging deformation vibrations respectively, of the methylene group. In both regions, several bands have been found to arise with increasing intensity when the molar content of ethylene in the chain is increased beyond 50 per cent; moreover, i.r. analysis in the melt state has shown clearly that these bands, as well as the previously reported ones, are not related to the crystallinity.

We deduce that the new bands should be related to new chain structures in which CH_2—CH_2 units are not isolated. As reported in Fig. 5 the melting points of copolymers having an ethylene molar content ranging from 50 to 82 per cent are well represented by a straight line satisfying the Eqn. (1):

$$1/T_m - 1/T_m^\circ = -\frac{R}{\Delta H_u} \ln X_A \tag{1}$$

(where X_A is the molar content of (—CH_2—CH_2—CF_2—CFCl—) units). This equation is valid for random-type copolymers in which only one type of unit is able to crystallize.[11] In our case, the crystallizable unit is (CH_2—CH_2—CF_2—CFCl), T_m° is the melting point of the corresponding homopolymer and T_m is the equilibrium melting temperature for copolymers in which the ethylene units, in excess over 1:1 molar ratio, act as randomly distributed impurities in the (—CH_2—CH_2—CF_2—CFCl—)$_n$ polymer chain. The enthalpy (ΔH_u) and the entropy (ΔS_u) of fusion for the (—CH_2—CH_2—CF_2—CFCl—) repeating unit have been calculated from the straight line of Fig. 5. These thermodynamic quantities for the entirely alternating copolymer are reported in Table 1, together with the corresponding values for polyethylene and polychlorotrifluoroethylene.

TABLE 1. THERMODYNAMIC QUANTITIES

Polymer	T_m° (°C)	ΔH_u (cal/mole)	$\Delta H_u/M_0$ (cal/g)	ΔS_u (cal deg^{-1} mol^{-1})	ΔS_u/bond (cal/deg)
Polyethylene	137·5*	960*	68·5*	2·34*	2·34*
Polychlorotrifluoroethylene	220–225†	1200*	10·3*	2·49*	1·25*
(—CH_2—CH_2—CF_2—CFCl—)$_n$	264‡	3176‡	22·0‡	5·91‡	1·97‡

* From Mandelkern.[5]
† From Hoffman and Weeks.[4]
‡ This work.

It must be pointed out that the fusion enthalpy values of crystalline polymers, determined by the copolymer melting method, were generally found to be lower than those obtained by the diluent method. This fact has been related to the difficulty of appreciating the disappearance of the last traces of crystallinity, which is higher in the copolymers than in the corresponding diluent-containing systems.[5] However, considering the particular technique and the sensitivity of the method adopted for our melting point determinations, the data reported in Table 1 appear to be fairly well comparable.

In Table 1 $\Delta H_u/M_o$ and ΔS_u/bond are also reported: they are the enthalpy of fusion per gram of crystalline polymer and the entropy of fusion per C—C bond, respectively. A useful comparison of these thermodynamic quantities for different polymers can thus be made.[5] For the completely alternating copolymer, these quantities are intermediate between those of the corresponding homopolymers: in particular, the entropy of fusion may indicate an intermediate flexibility of the new macromolecular chain in the liquid state.

As shown in our previous work,[1] the X-ray spectrum of the 1:1 copolymer is quite different from those of polyethylene and polychlorotrifluoroethylene while all the

copolymers of the present work displayed the same X-ray spectrum, apart from small variations in the Bragg distance of the principal peak, in the range 4·60–4·87 Å. This reflection is now attributed to side chain packing on the basis of preliminary X-ray analysis of oriented fibres, obtained by melt extrusion and then stretching at 120°. Moreover, a repeat distance of about 5 Å along the fibre axis seems to indicate a planar conformation of the main chain.

The degree of crystallinity of the copolymers is found to decrease with increasing ethylene content, as shown in Table 2: the data refer to compression moulded samples very slowly cooled after melting. A maximum crystallinity of 60 per cent was found for 1:1 copolymers.

TABLE 2. MELTING TEMPERATURE AND CRYSTALLINITY DEGREE OF ETHYLENE–CHLOROTRIFLUOROETHYLENE COPOLYMERS

Sample	Polymerization temperature (°C)	Composition (molar content) C_2H_4	Melting temperature (°C)	Crystallinity (%)
A	+60	50·00	206	—
B	0	49·65	243	45
C	−40	50·14	252	55
D	−78	50·00	264	60
E	−78	54·62	238	48
F	−78	58·18	213	35

In polychlorotrifluoroethylene, which is also highly crystalline,[4] a marked stereochemical irregularity was found[12] even although syndiotactic placement is preferred. Its high crystallizability was mainly related to high chain stiffness.[12] On the contrary, the high crystallizability of our 1:1 copolymer synthesized at −78° and characterized by a higher chain flexibility, should be attributed not only to a very regular alternation of the monomers but also to a high stereoregularity of the substituents along the chain.

The melting point and crystallinity of the 1:1 copolymers decrease by increasing the polymerization temperature (Table 2). Moreover, the i.r. spectra show that, when the polymerization temperature increases from −78°, new chain structures arise in addition to the alternating structure of CH_2—CH_2 and CF_2—CFCl units. In the region around 3 and 7 μ, the bands were found which have already been in copolymers having an ethylene molar content higher than 50 per cent: their intensities increase with the polymerization temperature. These results agree with the trend of the reactivity ratios with the temperature. The stereochemical regularity of the polymer chain is therefore decreased by increasing polymerization temperature.

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Résumé—Le point de fusion, la cristallinité et l'alternance des unités dans la chaîne des copolymères éthylène–chlorotrifluoroéthylène ont été étudiés par rapport aux compositions polymères et à la température de polymérisation. Des dosages ont été exécutés par des méthodes de tension ohmique, de rayons X et de microscopie optique. Une nouvelle unité de répétition est formée par une alternance régulière d'unités CH_2—CH_2 et CF_2—CFCl dans la chaîne polymère: elle peut se cristalliser selon une nouvelle constitution cristalline. Le point de fusion, l'entropie et l'enthalpie de la fusion des copolymères alternant complètement ont été établis. La température de polymérisation influe sur la régularité stéréochimique de la chaîne polymère.

Sommario—Il punto di fusione, la cristallinità e l'alternanza delle unità lungo la catena sono stati studiati per copolimeri etilene–clorotrifluoroetilene, in funzione della composizione e della temperatura di polimerizzazione. Sono stati utilizzati metodi roentgenografici, di spettroscopia in infrarosso e di microscopia ottica. È stato trovato che, per regolare alternanza delle unità CH_2—CH_2 e CF_2—CFCl nella catena del polimero, si origina una nuova unità di ripetizione che cristallizza secondo un caratteristico reticolo cristallino. Sono state determinate l'entalpia, l'entropia ed il punto di fusione del copolimero completamente alternato. La regolarità stereochimica della catena risulta influenzata dalla temperatura di polimerizzazione.

Zusammenfassung—An Äthylen-Chlortrifluoräthylen-Copolymeren wurde Schmelzpunkt, Kristallinität und Reihenfolge der Einheiten in der Kette in ihrer Beziehung zur Copolymerzusammensetzung und der Polymerisationstemperatur untersucht. Die Bestimmungen wurden ausgeführt mit IR-, Röntgen- und optisch-mikroskopischen Methoden. Durch regelmäßiges Alternieren von CH_2—CH_2 und CF_2—CFCl—Einheiten entlang der Kette wird eine neue wiederkehrende Einheit gebildet: sie kann nach einem neuen Kristallstrukturtyp kristallisieren. Es wurde der Schmelzpunkt und die SchmelzEntropie und Enthalpie des vollständig alternierenden Copolymeren bestimmt. Die Polymerisationstemperatur beeinflußt die stereochemische Regularität der Polymerkette.