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Vinylidene Fluoride Copolymers with Fluoroolefins

Giovanni Moggi[1], Piergiorgio Bonardelli[1], Claudio Monti[1] and Jan C. J. Bart[2]

[1] Montefluos C.R.S., Via Bonfadini 148, 20138 Milano, Italy
[2] Istituto G. Donegani, Via Fauser 4, 28100 Novara, Italy

SUMMARY

Copolymers of vinylidene fluoride (VDF) with fluoroolefins of the series CF_2CFX (X = F, Cl, Br, CF_3 and C_5F_{11}) have been synthesized in the 0-16 mole % CF_2CFX range. Results of physico-chemical characterisation by means of DSC techniques (T_g, T_M, ΔH_f) and X-ray diffraction are examined and related to the nature of the substituent of the fluoroolefin.
The T_g/T_M ratio varies from 0.5 for the VDF homopolymer to higher values at increased CF_2CFX content, although to a different extent for the various series of copolymers. The results show that the Beaman-Boyer empirical rule (T_g/T_M=2/3), developed for homopolymers, also applies to some copolymeric systems.

INTRODUCTION

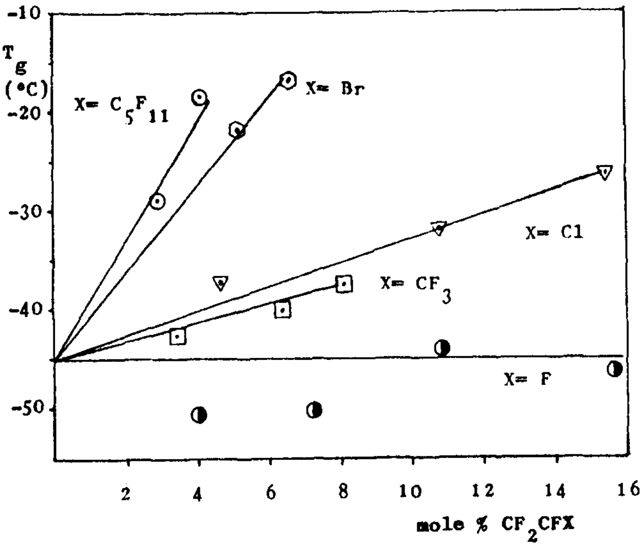
Whereas the T_g/T_M ratio has been studied for various homopolymers (BOYER 1975, 1977), no data have been published for copolymers. In this paper we report a preliminary study of the thermal behaviour, in terms of specific enthalpy of fusion (ΔH_f) and T_g/T_M ratio, of various vinylidene fluoride copolymers with CF_2CFX fluoroolefins (X = F, Cl, Br, CF_3, C_5F_{11})

EXPERIMENTAL

VDF CF_2CFX copolymers were synthesized by aqueous emulsion polymerisation. A 300 ml stainless steel autoclave was loaded with 100 ml demineralized water, 0.3 g ammonium persulphate and a monomer mixture up to attaining a pressure of 8-11 atm at 90°C. The monomer composition was adjusted in order to yield the desired polymer. The autoclave was then rocked until a pressure drop was observed. The low conversion allowed a narrow coposition distribution to be obtained. The polymer was coagulated by pouring the emulsion into a 2 % $Al_2(SO_4)_3$ solution under stirring, washed with demineralized water and dried at 45°C under vacuum for 7 hours. The sample composition was determined by elementary analysis and by ^{19}F NMR spectroscopy (for VDF-TFE, VDF-C_3F_6, VDF-C_7F_{14} and VDF-C_2F_3Cl) using a Varian EM 360 L spectrometer. X-ray diffraction (XRD) patterns of unoriented powder samples were recorded on a Philips PW 1050/1070 goniometer using Ni filtered Cu K radiation. Thermal analyses were run using a Perkin Elmer DSC-2C calorimeter with heating and cooling rates of 10 and 5°C/min, respectively.

RESULTS AND DISCUSSION

As shown in Fig. 1, T_g values for the various series of copolymers increase from -45.4°C (our experimental value for PVDF; literature values from -40 to -52°C according to DOHANNY and ROBB 1980, and SASABE et al. 1969) with an almost linear trend and a slope depending on the nature of the comonomer. In this context, it is to be considered that the low T_g value of PVDF is due to the identity of the 1, 1 substituents in the repeating unit (MOGGI et al. 1982).



; Fig. 1

Introduction of units in the polymeric chain results in a loss of simmetry and an increase in the T_g contribution of the VDF repeating unit. Moreover, interchain steric hindrance and the presence of bulky side groups also tends to increase the T_g value.

Starting from the observed melting point of 162°C for PVDF in our experimental conditions, as compared to literature value in the 154-184°C range (DOHANNY and ROBB), we notice a lowering of T_M, which is more pronounced for comonomers containing bulky side groups. The minor slope observed in the

VDF-TFE system may be interpreted on the basis of isomorphous substitution, which is very important for the preservation of long range order.

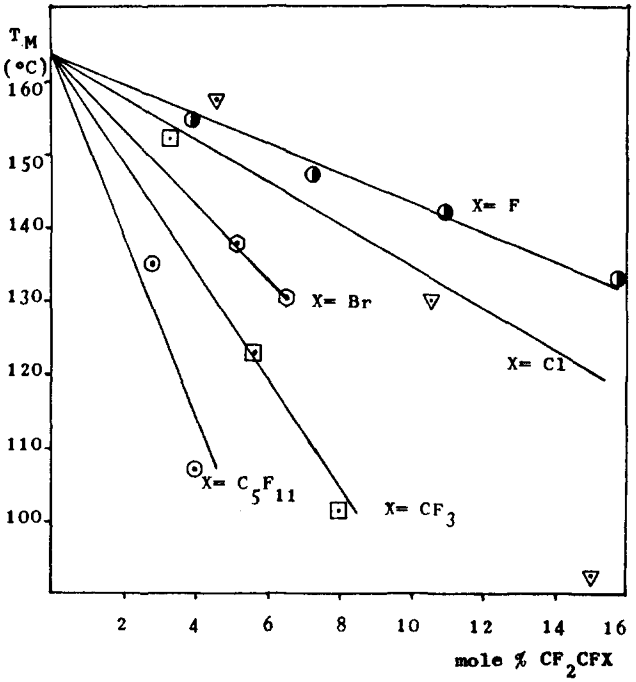


Fig. 2

On the whole, it is observed that sharp melting points disappear already in the thermograms of polymers of low comonomer content, for which some residual crystallinity still persists. Although the Beaman-Boyer empirical rule $T_g=(2/3)T_M$ is difficult to rationalize since T_g and T_M occur in different phases (amorphous for T_g and crystalline for T_M), the matter is simplified with Bunn's hypothesis that the same kinds of molecular motion occur at T_g and T_M (short range and long range, respectively). According to Boyer, T_g/T_M ratios take on values in three ranges (A, B and C, respectively): homopolymers without bulky side groups (such as PVDF) having T_g/T_M 0.5, most polymers (55%) having $T_g/T_M=0.667\pm0.05$, and those with long side chain (irrilevant for our purposes) with even higher values. By plotting T_g/T_M values vs comonomer content (Fig. 3) we notice a sharp trend away from the ratio (0.52) for the VDF homopolymer towards higher values with the slope depending on the size of the substituent group of the comonomer. In the case of $X=C_5F_{11}$ 4 mole % C_7F_{14} in the copolymer is already sufficient to shift the T_g/T_M ratio to about 0.66 (into Boyer's region B), apparently due to the strong contribution of the bulky side group. On the other hand, with a smaller substituent, such as Cl, as much as 15 mole % is needed to reach the same ratio value.

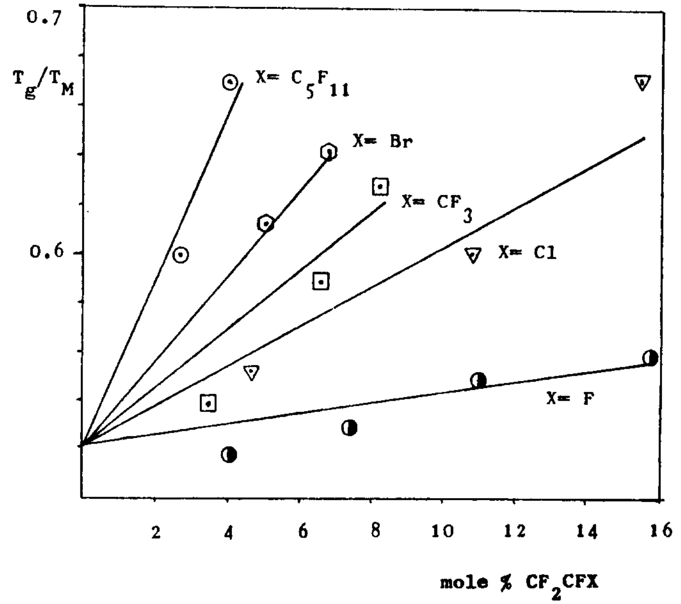


Fig. 3

No appreciable effect was noticed for X = F, probably as a result of isomorphous substitution (MOGGI et al., in press). It is stressed that the reported range of investigation is limited by difficulties in the determination of T_g and disappearance of T_M. We have further investigated the effect on specific enthalpy of fusion (ΔH_f) and degree of crystallinity of PVDF (measured by means of XRD) by introducing variable amounts of CF_2CFX comonomer in the polymeric chain (Fig. 4 and 5). Because of the uncertainties in the absolute value of the crystallinity of PVDF (literature reports a 35-65% range depending on the method of polymerisation and thermal history), both the crystallinity index and ΔH_f have been normalized with respect to the VDF homopolymer prepared in our experimental conditions. It is not unexpected that the observed trends as a function of the composition are similar for the crystallinity from XRD and ΔH_f. The isomorphous substitution in the VDF-TFE system again indoubtedly accounts for the minor variation observed for X = F. On the other hand, both the crystallinity and ΔH_f ratio decrease more rapidly with increase of bulkiness of the side groups. Little difference is observed for substitution of CF_3 and Br in the chain, as expected for the similar radii of these groups.

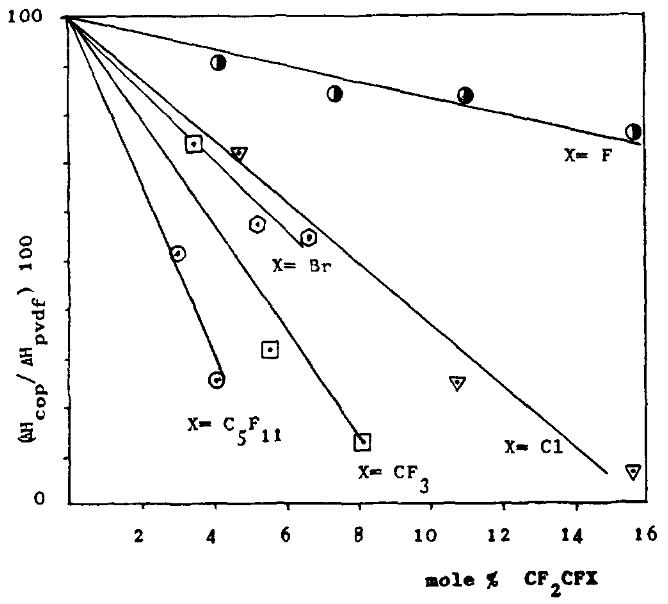

100
0
$(\Delta H_{cop}/\Delta H_{pvdf})$ 100
X= F
X= Br
X= C_5F_{11}
X= CF_3
X= Cl
2
4
6
8
10
12
14
16
mole % CF_2CFX

Fig. 4

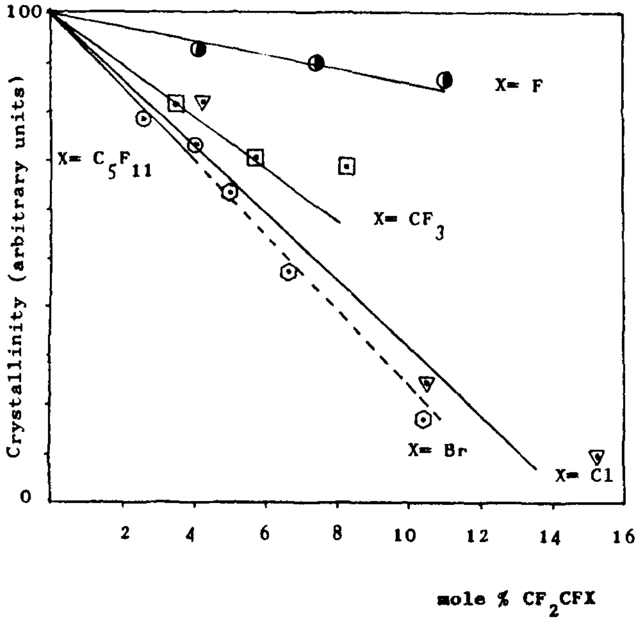

100
0
Crystallinity (arbitrary units)
X= F
X= C_5F_{11}
X= CF_3
X= Br
X= Cl
2
4
6
8
10
12
14
16
mole % CF_2CFX

Fig. 5

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