New isomers of poly(vinyl fluoride) with controlled regiosequence microstructure

Rudolf E. Cais and Janet M. Kometani
AT&T Bell Laboratories, Murray Hill, New Jersey 07974, USA
(Received 1 May 1987; accepted 13 June 1987)

The addition polymer of vinyl fluoride, PVF, contains head-to-head and tail-to-tail structural irregularities (regiosequence defects) caused by monomer reversals during chain propagation. Previously no method existed for significantly altering the level of regiosequence defects, which typically amounts to 10% reverse addition and changes little with polymerization temperature. We report here a novel synthetic procedure which enables us to adjust this defect level by reductive dechlorination of precursor copolymers of vinyl fluoride, VF, with suitable chlorofluoroethylenes, using tributyltin hydride to replace chlorine quantitatively with hydrogen. The products are regioisomers of PVF with defect levels depending on the identity of the chlorofluoroethylene monomer, and the composition of the precursor copolymer, which is selected by adjusting the comonomer feed ratio. Reduction of VF copolymers with vinylidene chlorofluoride yields PVF with defect levels in the range 0–10%, whereas reduction of VF copolymers with 1-chloro-2-fluoroethylene yields PVF with 10–30% defects. We measure the regiosequence distribution of these various PVF isomers by 470 MHz ^{19}F nuclear magnetic resonance, and show that the polymers are stereoirregular (atactic) as well. The crystalline melting temperature of PVF increases as the polymer becomes more isoregic.

(Keywords: poly(vinyl fluoride); regiosequence microstructure; head-to-head defects; tail-to-tail defects; reductive dechlorination; fluorine-19 n.m.r.)

INTRODUCTION

Polyfluoroethylenes may exhibit regiosequence isomerism if the olefinic carbons of the corresponding monomers have different substitution patterns. This is the case for vinyl fluoride (VF), vinylidene fluoride (VF_2) and trifluoroethylene (F_3E), but not for 1,2-difluoroethylene and tetrafluoroethylene. Indeed, as normally prepared, PVF, PVF_2 and PF_3E are regioirregular, with around 10, 5 and 12% reversed monomer units, respectively[1-3]. These structural irregularities influence chemical and physical properties. However, the extent of head-to-head and tail-to-tail addition varies little with polymerization temperature[4], and previously there has been no way to significantly control this level of aregic structure in polyfluoroethylenes.

We have had an ongoing interest in the regiosequence microstructure of polyfluoroethylenes, as this field presents many interesting challenges in polymer synthesis, characterization and statistical analysis. Initially we devised a general procedure to prepare PVF [1], PVF_2 [5] and PF_3E [3] free of head-to-head and tail-to-tail monomer junctions, and we denoted these pure head-to-tail regiosequence isomers as isoregic[2]. Also we described the alternating copolymerizations of selected comonomer pairs to produce pure head-to-head, tail-to-tail regiosequence isomers of the above polymers, which we have termed syndioregic[1,3]. Subsequently we discovered an interesting deuterium isotope effect on the level of aregic sequences in PVF_2 [6].

High-resolution ^{19}F nuclear magnetic resonance (n.m.r.) spectroscopy was employed in all cases to characterize the regiosequence microstructures in detail, and we have developed a formal statistical analysis to describe the sequence distribution by analogy with binary copolymerization[2]. Recently we reported a logical development of these synthetic procedures to access a wide range of regiosequence isomers for PVF_2[7], and here we illustrate the utility of the procedure by adapting it to the PVF system.

Our general strategy for adjusting the level of reverse additions in polyfluoroethylenes starts with the synthesis of a precursor copolymer involving the desired fluoroethylene monomer and an appropriate comonomer having a directing substituent (such as Cl). The precursor copolymer is then reductively dechlorinated with tributyltin hydride, which replaces the directing substituent with hydrogen, thereby creating a regioisomer of the polyfluoroethylene in question. Fluorine does not react under the conditions chosen for removal of chlorine, so that the integrity of the fluorine substitution pattern is maintained. The extent of reversals is adjusted by varying the comonomer feed ratio, which alters the composition of the precursor copolymer. In the present case there are two options, unique to PVF: the comonomer can be chosen to increase (CHCl=CHF) or decrease (CH_2=CFCl) reverse addition.

EXPERIMENTAL

Materials

Commercial poly(vinyl fluoride) (C-PVF) was obtained from Aldrich Chemical Company. The preparation of isoregic PVF by reductive dechlorination of poly(vinylidene chlorofluoride) (R-100-VCF) has been described previously[1].

Synthesis of precursor copolymers

Vinyl fluoride (VF) was obtained from the Matheson gas company. Vinylidene chlorofluoride (VCF) and 1-

0032-3861/88/010168-05$03.00

chloro-2-fluoroethylene (CFE) were supplied by the SCM Speciality Chemical company. These fluoroethylene monomers were dried by passage through columns packed with silica gel and molecular sieves, then degassed and fractionally distilled under vacuum. The polymerization initiator was trichloroacetyl peroxide (TCAP), which was prepared from trichloroacetyl chloride and sodium peroxide according to a standard procedure[8]. The TCAP was transferred into glass reaction tubes as a solution in 1,2-dichlorotetrafluoroethane, which was then evaporated to dryness at −80°C.

Appropriate comonomer mixtures were prepared by condensing measured quantities of the respective monomers in the gas phase into the reaction tube at liquid nitrogen temperature. The tube was sealed under vacuum and warmed to mix the monomers and dissolve the crystalline initiator. Bulk copolymerizations were allowed to proceed at 0°C for a suitable period, after which the tubes were cut open and the residual monomer removed under vacuum. The copolymers were dissolved and reprecipitated in methanol before being dried in a vacuum oven for approximately 18 h.

Reductive dechlorinations

Reductive dechlorination of the precursor copolymers was done at 60°C in tetrahydrofuran containing a 50% molar excess (with respect to chlorine) of tri-n-butyltin hydride with periodic addition of azobis(isobutyronitrile) initiator. Owing to the relative inefficiency of initiation[9], up to 50 mol% of azobis(isobutyronitrile) relative to chlorine was necessary. The VF–CFE copolymers were dechlorinated after 40 h, but it was not possible to remove all the chlorine from VF–VCF copolymers by the above procedure. Accordingly, a second-pass reduction was required for these precursors for 40 h under more forcing conditions, using dimethylacetamide as solvent at 80°C. The elimination of chlorine could be monitored by ^{19}F n.m.r. (see below), but X-ray fluorescence spectroscopy provided a more convenient test, especially for the trace levels present at the final stage of reduction.

Characterization

High-field ^{19}F n.m.r. spectra were observed at 470.7 MHz on a Jeol GX-500 spectrometer with a 30 kHz sweep width and 32K data points. The polymers were dissolved in dimethylformamide-d_7 at 135°C. About 1000 transients were accumulated with an acquisition time of 0.54 s and a pulse delay of 3.5 s, using a pulse width of 8.0 μs for a 90° flip angle. Protons were decoupled by broad-band irradiation centred at 500 MHz. Chemical shifts are referenced to internal hexafluorobenzene, which is assigned a value of −163 ppm with respect to $CFCl_3$. The melting points of the series of PVF isomers were obtained by observing the melting endotherm on a DuPont 1090 thermal analyser with a d.s.c. cell.

RESULTS AND DISCUSSION

Synthesis and reduction of precursor copolymers

Table 1 gives synthetic details for the range of precursor copolymers of VF with either VCF or CFE that was examined in this work. The bulk copolymerization rate is accelerated by VCF but inhibited by CFE. This is consistent with our prior observation that the homopolymerization rate of VCF is much more rapid than that of CFE. The 1,2-substitution pattern of the double bond in CFE is not favourable for facile addition polymerization.

Table 1 Details of copolymerizations of VF with VCF and CFE at 0°C with 0.5 mol% trichloroacetyl peroxide initiator

Sample designation	VF in feed (mol%)	Polymerization time (h)	Polymerization yield (wt%)
50-VCF	50	17	74
40-VCF	60	18	58
30-VCF	70	18	49
20-VCF	80	18	23
10-VCF	90	18	23
10-CFE	90	40	8
20-CFE	80	64	10
30-CFE	70	64	8
40-CFE	60	64	6
50-CFE	50	65	4

The precursor copolymers were generally amorphous and readily soluble in acetone, tetrahydrofuran, dimethylformamide and dimethylacetamide. However, during reductive dechlorination in tetrahydrofuran the solubility of the product decreased as its composition approached that of PVF. This was most pronounced for the highly isoregic samples (from VF–VCF copolymers), and prevented quantitative removal of chlorine by the one-pass procedure as noted above. In particular, ^{19}F resonances at −177.6 and −178.0 ppm, which we assign to the central fluorine in –CFCl–CH_2–CHF–CH_2–CHF– sequences, were indicative of incomplete chlorine removal. A more sensitive and convenient test for trace amounts of chlorine was provided by X-ray fluorescence spectroscopy, which was used to monitor the final stages of reduction and indicate the necessity of a second-pass reduction in the case of VF–VCF copolymers.

The more aregic PVF samples had better solubility owing to two factors. First, their molecular weights were lower (as observed by solution viscosity) because of inhibition of the copolymerization rate by CFE (note yields in *Table 1*), so that chain termination competed more readily with the propagation steps. Second, the amorphous fraction increased and the melting point was depressed as the PVF samples became more aregic (see below).

Analysis by 470.7 MHz ^{19}F n.m.r.

Figure 1 shows the ^{19}F spectra for two reduced VF–VCF copolymers and compares these with the spectrum from pure isoregic PVF. The spectra consist of two distinct regions: one from −179 to −183 ppm, corresponding to the –CH_2–CHF–CH_2– regiosequence triad, and one from −189 to −199 ppm, corresponding to the –CH_2–CHF–CHF– regiosequence triad. Following our convention introduced for describing regiosequences[2], we denote these as the A_3 and B_3 triads, respectively. The triad and pentad regiosequences are defined in *Table 2*, using a binary notation to represent the –CH_2– carbon by 0 and the –CHF– carbon by 1 (the numbers designate the number of fluorines attached to a particular carbon centre). Only the set of 1-centred sequences with an odd number of carbons can be observed by ^{19}F n.m.r. The aregic defect level is monitored by the relative area of the upfield B_3 resonances. The B_3 area is zero for the pure isoregic

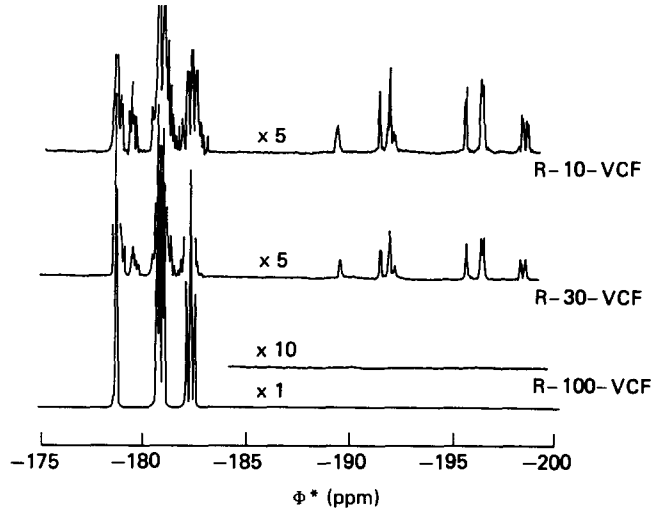

Figure 1 470.7 MHz ^{19}F n.m.r. spectra of PVF isomers prepared by quantitative reductive dechlorination of precursor copolymers 10-VCF, 30-VCF and 100-VCF. Incomplete removal of chlorine results in a group of resonances around −177.5 ppm from the –CFCl–CH_2–CHF–CH_2–CHF– sequence

Table 2 Set of regiosequence triads (S_3) and pentads (S_5) observed by ^{19}F n.m.r. for PVF

Notation	Sequence[a]
A_3	010
B_3	011
A_5	10101
B_5	00101
C_5	10110
D_5	00110

[a] 0=–CH_2–, 1=–CHF–

sample as expected, and increases as the mol% of VCF in the precursor copolymer decreases.

Figure 2 shows the same regions for the commercial PVF sample and two reduced VF–CFE copolymers. Here the B_3 defect resonances are even more prominent, and their relative intensity increases with increasing CFE content in the precursor copolymers. The spectra in *Figures 1* and *2* do not disclose any features not present in commercial PVF, and differ only in the relative proportions of the various regiosequences, so that all reduced copolymers are genuine PVF isomers. As mentioned above, the only anomalous resonances were observed from residual chlorine when the reduction was incomplete.

Figure 3 shows an expansion of the A_3 region with assignments for the A_5 and B_5 pentad regiosequences. The isoregic sequence is well resolved into the isotactic, heterotactic and syndiotactic stereosequences in order of increasing field strength. Each of these peaks is split in turn by pentad fine structure. All ten stereosequence pentads are resolved, including the mm-centred set, which was not split at a lower observing frequency of 188.2 MHz[1]. This fine structure has been assigned previously; in particular, two-dimensional J-correlated (COSY) n.m.r. has confirmed all assignments at the stereosequence and regiosequence pentad level[10].

All pentad stereosequence fine structure can be resolved when the samples are highly isoregic (e.g. sample R-20-VCF), but this is obscured by broadening when the aregic defect content increases (e.g. sample R-40-CFE). This broadening results from a sensitivity to high-order regiosequence heptad fine structure, but its effect cannot be separated from the structural non-equivalence involving tacticity. For example, the B_5 sequence is split into two main regions according to dyad tacticity (m and r), with additional longer-range fine structure. If the samples were stereoregular then it would be possible to resolve these higher-order regiosequences.

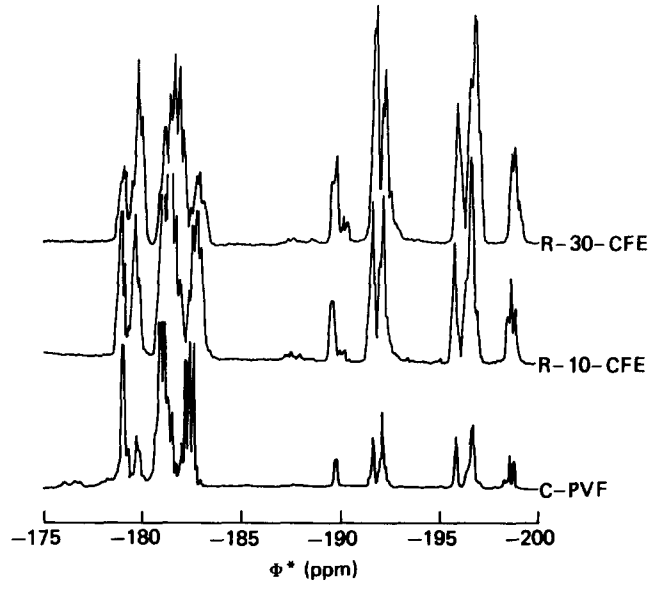

Figure 2 470.7 MHz ^{19}F n.m.r. spectra of commercial PVF (C-PVF) and the isomers prepared by quantitative reductive dechlorination of precursor copolymers 10-CFE and 30-CFE

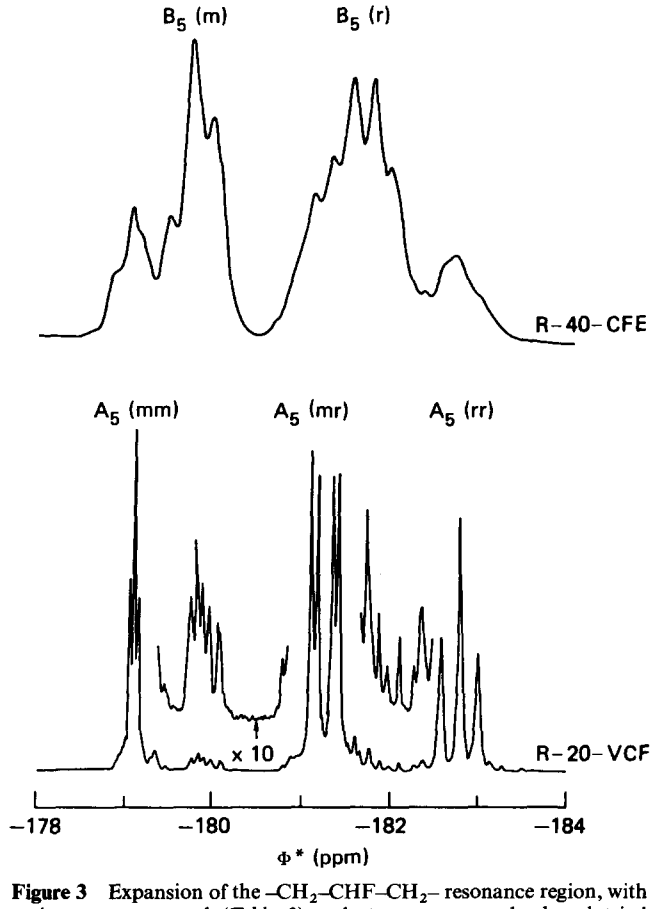

Figure 3 Expansion of the –CH_2–CHF–CH_2– resonance region, with regiosequence pentad (*Table 2*) and stereosequence dyad and triad assignments from ref. 10

Figure 4 shows the expansion of the upfield B_3 defect region with regiosequence pentad and stereochemical dyad and triad fine structure. The assignments indicated on the figure are those verified by Bruch *et al.* using 2D n.m.r.[10] Two types of stereochemical dyads must be considered: one involving the pair of asymmetric carbons in the –CHF–CHF– junction (which exhibit M or R relative stereochemistry), and the more typical arrangement for vinyl polymers involving the –CHF–CH_2–CHF– segment (m or r). The broadening of peaks with increasing defect content is apparent in this region as well, owing to higher-order heptad regiosequences.

Quantitative analysis of defect content

The definition of a 'defect' is somewhat arbitrary. If the polymer is predominantly isoregic, then irregular or defect structures involve the head-to-head and tail-to-tail linkages 1–1 and 0–0, respectively. Defects are counted at the dyad regiosequence level, so that 00 and 11 may be viewed as 'irregular' dyads and 01 and 10 may be viewed as 'regular' dyads, if the latter species are more numerous. The number of such defects may be normalized with respect to the number of bonds formed between monomer units by polymerization. This is a monomer-based definition which is related to the number of times the monomer unit switches direction during chain propagation. Alternatively a structure-based definition may be used where the number of defects is normalized over the total number of bonds between backbone carbons.

For a two-carbon monomer like VF there are twice as many backbone bonds as linkages formed by addition polymerization. It follows that within the set of dyad probabilities the chance of finding a bond created by the linkage of two monomer units (0–1 or 1–0) is one half, and the chance of finding a bond between backbone carbons (0–0, 0–1, 1–0 and 1–1) is unity. If both 00 and 11 dyads are counted as defects, the probability of a defect will be $2\{p(00)+p(11)\}$ when normalized over the number of monomer linkages, and $p(00)+p(11)$ when normalized over the number of backbone bonds. Here the unconditional probability of occurrence of a particular dyad regiosequence is denoted by p(dyad).

We use the latter definition here for the reasons set out

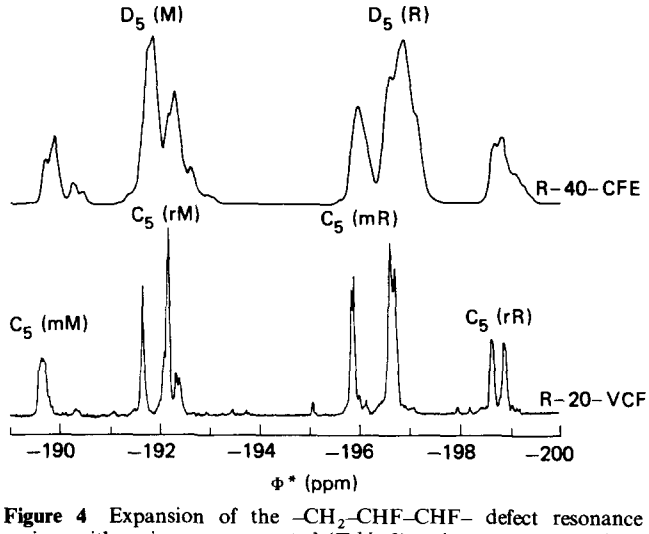

Figure 4 Expansion of the –CH_2–CHF–CHF– defect resonance region, with regiosequence pentad (*Table 2*) and stereosequence dyad and triad assignments from ref. 10

Table 3 Unconditional probabilities of the four observed regiosequence pentads and the corresponding defect content for PVF isomers

Regioisomer	Sequence probability A_5	B_5	C_5	D_5	% Defect[a]
R-100-VCF[b]	0.5	0	0	0	0
R-50-VCF	0.4809	0.0069	0.0069	0.0054	1.2
R-40-VCF	0.4648	0.0136	0.0136	0.0080	2.2
R-30-VCF	0.4588	0.0155	0.0155	0.0102	2.6
R-20-VCF	0.4346	0.0249	0.0249	0.0155	4.0
R-10-VCF	0.3967	0.0385	0.0385	0.0262	6.5
C-PVF[c]	0.3392	0.0573	0.0573	0.0462	10.3
R-10-CFE	0.2215	0.0949	0.0949	0.0887	18.4
R-20-CFE	0.1092	0.1329	0.1329	0.1250	25.8
R-30-CFE	0.0829	0.1365	0.1365	0.1440	28.0
R-40-CFE	0.0640	0.1399	0.1399	0.1562	29.6
R-50-CFE	0.0714	0.1397	0.1397	0.1491	28.9

[a] % Defect $= 100\{P_{obs}(C_5)+P_{obs}(D_5)\}$
[b] Isoregic sample by reduction of PVCF[1]
[c] Commercial PVF sample

in our previous statistical analyses of regiosequence distributions[3]. Therefore the aregic PVF samples are analysed according to:

$$\% \text{ defect} = 100\{p(00)+p(11)\}$$

It can be shown[2] that $p(00)+p(11)$ is equal to $P_{obs}(B_3)$, which is the B_3 resonance area divided by twice the area of all ^{19}F resonances. The factor of two arises because the 011 triad probability must be normalized over all triads, which include the 0-centred sequences 101 and 100, which are not observed by ^{19}F n.m.r. The results from this analysis are shown in *Table 3*.

Terpolymerization scheme

The polymerization of VF may be regarded as a pseudo-copolymerization involving two monomers differing only in their orientation with respect to the growing chain end. Under typical conditions one orientation is more reactive, so that only 10.3% of reverse units are built into the chain. *Table 3* shows that the comonomer VCF dilutes this level of reverse addition, whereas the comonomer CFE enhances this level in the reduced polymers. The homopolymerizations of VCF and CFE are regioregular[1], with the propagating radical centred on the chlorinated sp^2 carbon. We may therefore represent the formation of the PVF precursors as terpolymerizations:

With VCF:

$$(CH_2{=}CHF)_m+(CHF{=}CH_2)_n+(CH_2{=}CFCl)_p\rightarrow$$
$$\text{--}(CH_2\text{–}CHF\text{–})_x\text{–}(CHF\text{–}CH\text{–})_y\text{–}(\text{–}CH_2\text{–}CFCl\text{–})_z\text{--}$$

With CFE:

$$(CH_2{=}CHF)_m+(CHF{=}CH_2)_n+(CHF{=}CHCl)_p\rightarrow$$
$$\text{--}(CH_2\text{–}CHF\text{–})_x\text{–}(CHF\text{–}CH_2\text{–})_y\text{–}(\text{–}CHF\text{–}CHCl\text{–})_z\text{–}$$

The actual sequence distribution will be statistical and not block as represented by these equations. Both VF monomer orientations are equiprobable so the m/n ratio is 1. However, the ratio x/y depends on reactivity ratios

and will vary with polymerization temperature; as we have seen, a typical value for PVF is approximately 9/1. The key feature of these synthetic schemes is that the monomer feed ratio $(m+n)/p$ can be varied, thereby controlling the ratio of forward to reverse addition, which is either $(x+z)/y$ (for reduced VF–VCF copolymers), or $x/(y+z)$ (for reduced VF–CFE copolymers).

The sequences A_5 and B_5 overlap strongly so it is difficult to measure their separate areas, particularly at high defect levels. However the C_5 sequence is always well resolved (*Figure 4*), and its probability is readily obtained. Furthermore, the relationship $P_{obs}(B_5)=P_{obs}(C_5)$ holds true for any sequence statistics[2], so that

$$P_{obs}(A_5)=P_{obs}(A_3)-P_{obs}(C_5)$$

All regiosequence pentad probabilities $P_{obs}(S_5)$ were derived using these identities and their values are shown in *Table 3*.

Melting temperatures

The level of regiosequence defect structure strongly affects the physical properties of PVF. The plot in *Figure 5* shows that the melting point of the crystalline fraction decreases rapidly as the polymer becomes more aregic, and levels out at around 158°C. There is a concomitant decrease in extent of crystallinity and increase in solubility, as noted previously. It is not surprising that the isomers with greatest structural disorder are more amorphous. However, the n.m.r. spectra show that all samples are stereoirregular, and an even greater degree of crystallinity should be possible for isotactic, isoregic PVF. This degree of structural perfection has yet to be realized.

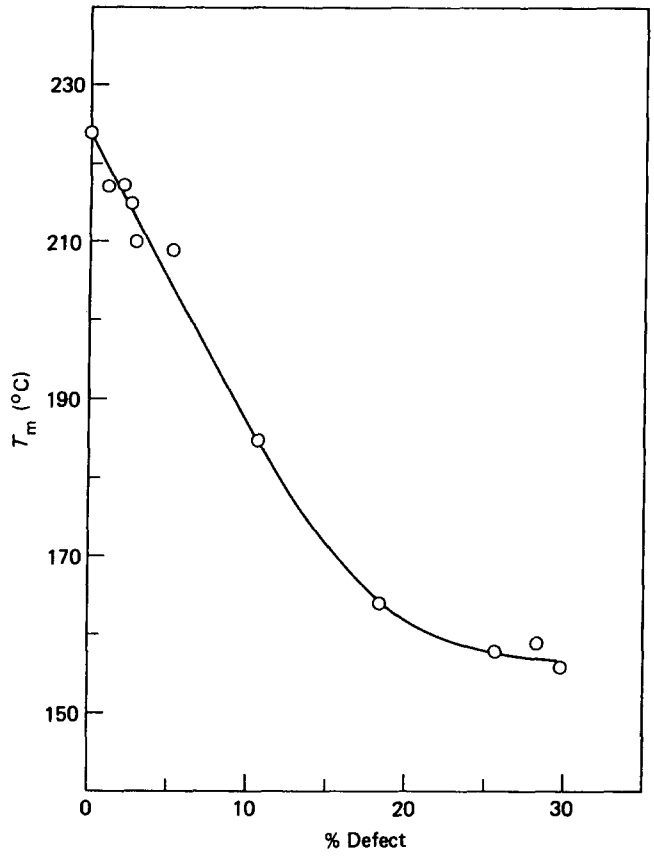

Figure 5 Melting points of PVF regioisomers as a function of defect content

REFERENCES

1 Cais, R. E. and Kometani, J. M. in 'NMR and Macromolecules' (Ed. J. C. Randall), *Am. Chem. Soc. Symp. Ser.* 1984, **247**, 153
2 Cais, R. E. and Sloane, N. J. A. *Polymer* 1983, **24**, 179
3 Cais, R. E. and Kometani, J. M. *Macromolecules* 1984, **17**, 1932
4 Gorlitz, M., Minke, R., Trautvetter, W. and Weisgerber, G. *Angew. Makromol. Chem.* 1973, **29/30**, 137
5 Cais, R. E. and Kometani, J. M. *Org. Coat. Appl. Polym. Sci. Proc. Am. Chem. Soc.* 1983, **48**, 216
6 Cais, R. E. and Kometani, J. M. *Macromolecules* 1984, **17**, 1887
7 Cais, R. E. and Kometani, J. M. *Macromolecules* 1985, **18**, 1354
8 Young, D. M. and Stoops, W. N. US Patent 2 792 423, 1957
9 Beckwith, A. L. J. and Pigou, P. E. *Aust. J. Chem.* 1986, **39**, 77
10 Bruch, M. D., Bovey, F. A. and Cais, R. E. *Macromolecules* 1984, **17**, 2547