Effects of chain structure on the melting characteristics of poly(vinyl fluoride)

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(Received 21 July 1992; revised 29 September 1992)

The effects of configurational disorder and chain branching on the melting characteristics of the addition polymer poly(vinyl fluoride) (PVF) have been investigated. For PVF, the melting point (T_m) was found to be strongly dependent on polymerization temperature, and only weakly dependent on polymerization pressure. Structural investigation of the polymer backbone using ^{19}F nuclear magnetic resonance analysis reveals that the pronounced increase in T_m results predominantly from a decrease in chain branching and, to a far lesser extent, from improved main-chain regio-regularity. For PVF with a (tertiary fluorine) branch-point content above 2.2% (~ one branch per 45 monomer additions) the melting point is reduced to below 180°C, whereas for samples with branch-point content less than 0.3% (~ one branch per 300 monomer additions) the melting point lies above 205°C. Moreover, for the same polymers, the number of head-to-head monomer linkages was found to remain largely constant ($= 12.5 \pm 1\%$).

(Keywords: polymer melting; chain branching; regio-sequence; ^{19}F nuclear magnetic resonance; head-to-head defects; poly(vinyl fluoride))

INTRODUCTION

Spectroscopic studies of configurational disorder in polyfluoroethylenes remain an area of intensive interest. Indeed, numerous studies of the microstructure of poly(vinyl fluoride) (PVF)[1–9] and poly(vinylidene fluoride) (PVF_2)[1,7,10–12] have been reported. Undoubtedly this work has been motivated by the unique chemical and physical characteristics of these polymers; i.e. on the one hand their properties can be intermediate between those of polyethylene and polytetrafluoroethylene, and on the other hand they can be quite distinct, e.g. piezoelectric and pyroelectric properties of PVF_2 (ref. 13). In addition, conventional approaches for preparing polyfluoroethylenes, generally involving free-radical polymerizations, often lead to a broad range of material behaviour, the nature of which depends on the character of the defects incorporated into the polymer chain.

For homopolymers of PVF, two types of configurational disorder are possible: stereo-irregularity and regio-irregularity. With respect to the former case, previous nuclear magnetic resonance (n.m.r.) studies[1–5,7] and infra-red spectroscopy[8,9] have clearly established that PVF is largely stereo-irregular, irrespective of the polymerization conditions used to prepare the polymer. That is, detailed stereo-sequence assignments show that the polymer is predominantly atactic, with only a modest dominance of syndiotactic sequences.

Moreover, for PVF (like PVF_2), monomer linkages can occur at either of the chemically distinct olefinic carbons. Hence, by adding monomers in either a head-to-head ($-CH_2CHF-CHFCH_2-$) or head-to-tail ($-CH_2CHF-CH_2CHF-$) fashion, varying extents of regio-ordering in the polymer chain are possible. In contrast, no similar structural disorder can develop in neat polymers of 1,2-difluoroethylene or polytetrafluoroethylene, where the addition of a monomer at either 'end' is chemically identical.

The importance of regio-ordering in PVF has received considerable attention. Most of these studies, employing ^{19}F n.m.r. analysis, have centred on elucidating the role of head-to-head defects in governing the melting characteristics, crystallinity and solubility of the polymer. Wilson and Santee[7], in addition to providing the first clear evidence of head-to-head defects in PVF, also showed that head-to-head additions (i.e. monomer reversals) comprised roughly one out of every six monomer linkages. Subsequent studies by Caporiccio *et al.*[2] and Goerlitz *et al.*[1] provided additional support for the n.m.r. assignments. In addition, Caporiccio *et al.* showed that the frequency of head-to-head additions was only a weakly increasing function of the polymerization temperature.

In other work, Cais and Kometani[3] used a novel synthetic approach for controlling the regio-ordering in PVF. Here, a range of PVFs was made via a reductive dechlorination of *precursor* copolymers, prepared from VF and chlorofluoroethylenes. By adjusting the defect level of the precursors, regio-isomers of PVF with head-to-head contents from 0% (i.e. isoregic) to 30% could be prepared. In addition to determining the regio-regularity, ^{19}F n.m.r. analysis was used to establish that as-produced isomers, too, were largely stereo-irregular. Consequently, Cais and Kometani argued that the melting point (T_m) of these PVFs, which differed by as much as 60°C, was governed solely by differences in

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the regio-ordering of the polymer. For the isoregic PVF, they observed that T_m approached 220°C, whereas for PVF with a head-to-head level of 30%, T_m decreased to ca. 158°C.

Other support for the dominant role of regio-ordering in controlling the polymer melting point has been suggested from the studies of Lando and Hanes[14]. In that work, wide-angle X-ray scattering and molecular modelling were used to determine the head-to-head content of PVF from the ratio of the intensities of the 0 0 1 to 0 0 2 structure factors, and its apparent correlation with the melting behaviour. However, much of this analysis is based on the dubious assumption that a head-to-head defect is invariably followed by a tail-to-tail defect.

Even more importantly, however, it should be noted that in this study, as well as in the work of Cais and Kometani[3], the likely role of chain branching in influencing the polymer melting point was not addressed. Despite the earlier work of Goerlitz *et al.*[1], who reported on the unequivocal presence of chain branches in PVF, no further investigation of their role in affecting melting had been pursued. Recently, however, Ovenall and Uschold[6] have used high-resolution n.m.r. techniques to investigate quantitatively chain branching in PVF. By varying polymerization conditions, Ovenall and Uschold found that the extent of chain branching in PVF could be controlled; generally lower polymerization temperatures and higher polymerization pressures favoured more linear polymer. In contrast, over the same range of conditions, the number of head-to-head defects remained largely invariant. These workers also observed that both the polymer melting point and crystallinity increased strongly with a decrease in chain branching. On the other hand, no such correlations with head-to-head defects were observed. While this study clearly illustrated the importance of chain branching in PVF, the narrow range of experimental conditions explored did not permit a quantitative relationship between branch points and melting to be established.

In this study, the critical role of chain branches in influencing the melting characteristics of PVF is further examined. Here we report on the melting behaviour of PVFs prepared over a broad range of polymerization conditions. Using high-resolution ^{19}F n.m.r. analysis, the extents of regio-regularity and chain branching in each of these polymers are examined, and their importance in governing the melting behaviour of PVF is discussed.

EXPERIMENTAL

Polymer preparation

Following procedures previously reported, PVF samples were prepared by free-radical polymerizations of high-purity VF in aqueous dispersions[15,16]. Two different reactor systems, one batch and the other a continuous process, were used. They are described below.

Batch reactor (400 ml shaker tubes). A series of polymers were prepared at polymerization temperatures ranging from 40 to 90°C, and at polymerization pressures from 900 to 15 000 psi (~6.2 to 103 MPa). A charge of ca. 200 ml water, 100 g VF and 0.10 g initiator (0.05 g at 12 000 and 15 000 psi) was used for all of the polymerizations. By adjusting the polymerization times at each polymerization temperature, a VF conversion of 35–50% could be achieved. The as-produced PVF/slurry was dried in a centrifuge to increase the solids content from ca. 15–20 wt% to greater than 50 wt%, and then heating the centrifuged material to 95°C in a hot-air oven for 2 h to reduce the final water concentration to less than 0.5 wt%.

Small-scale continuous reactor. Another series of PVFs were prepared in a one-litre continuous reactor system. With this reactor the water and VF streams were separately introduced and the VF was dispersed into small droplets through agitator mixing. By controlling the agitator speed, polymers could be prepared over a wide range of conditions. In all cases polymerizations were run with a VF conversion of 30–50%. Similar drying procedures were employed here.

^{19}F n.m.r. spectroscopic analysis

Structural analysis of PVF was performed with ^{19}F nuclear magnetic resonance. Samples were prepared by heating a 25 wt% solution of PVF in dimethylacetamide (DMAc) to 160°C for 15 min to swell the PVF. N.m.r. measurements were made with a Bruker AC-250 high-resolution spectrometer operating at 235 MHz for fluorine n.m.r. The fluorine free induction decays were collected at 130°C following a 90° pulse without proton decoupling with 20 s cycle time between pulses. At least 256 scans were collected for each spectrum.

A typical ^{19}F n.m.r. spectrum of PVF is shown in *Figure 1*. The spectra were referenced by taking the chemical shift of the major high-frequency feature as −179 ppm, where 0 ppm corresponds to the resonance feature of CFC13 (Freon 11)[4]. The major group of resonance features in the ^{19}F n.m.r. spectrum of PVF between −178 and −182 ppm have been assigned to head-to-tail monomer units, while the minor group of resonance features between −189 and −197 ppm have been assigned to head-to-head monomer units[5]. Additionally, following the analysis of Ovenall and Uschold, the weak resonance features in the spectrum of PVF near −220, −147 and −162 ppm have been assigned to CH_2F end groups, tertiary fluorine atoms originating from head-to-tail monomer units and tertiary

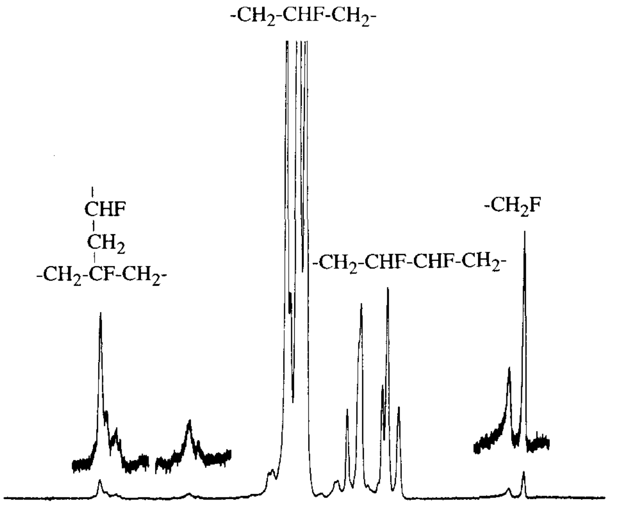

Figure 1 The 235 MHz ^{19}F n.m.r. spectrum of PVF in dimethylacetamide. The structural units associated with the resonances are indicated

fluorine atoms originating from head-to-head monomer units, respectively. These structural units are illustrated in *Figure 1*.

Differential scanning calorimetry

A Mettler 30 differential scanning calorimeter (d.s.c.) was used to determine the melting point and crystallinity of the PVF samples. In all cases, samples were heated at a rate of 10°C min^{-1} and the melting endotherms recorded. Values of crystallinity reported here are based on a ΔH_f of 164 J mol^{-1} for PVF.

EXPERIMENTAL RESULTS

Polymerization temperature

For PVF samples polymerized in the batch reactor, *Figure 2* shows the dependence of the melting point (T_m) on the isothermal polymerization temperature. In each case polymerizations were run at a pressure of 8000 psi (~55 MPa). For polymers prepared at 90°C, T_m was found to be 186°C, and as the polymerization temperature was decreased, T_m increased nearly monotonically, reaching $T_m = 206$°C for PVF polymerized at 40°C. These results are in qualitative agreement with those previously reported[6] for samples that were also prepared at 8000 psi, but in a large-scale continuous reactor (○). In that case, too, the melting point was observed to increase steadily from 187 to 197°C as the polymerization temperature was decreased from 102 to 80°C. It can also be seen that, while the slopes of the two curves are similar, at comparable polymerization temperatures the polymers prepared in the batch process exhibited a lower melting point. As will be described below, these differences have their origin in microstructural differences in the polymer backbone.

In addition to increasing the nominal peak melting point of PVF, decreasing the polymerization temperature was found to narrow the breadth of the melting endotherm. This feature is illustrated in *Figure 3*, which is a comparison of the melting endotherms for two PVF samples prepared in the batch reactor, one at 40°C and the other at 90°C. It is evident that decreasing the polymerization temperature not only increases the polymer melting point, but also accompanies a substantial decrease in the fraction of low-melting crystals. Moreover, based on a value $\Delta H_f = 164$ J mol^{-1} for PVF, a quantitative integration of the melting endotherms for these samples along with those prepared over the entire range reveals that the sample crystallinity increases slowly with decreasing polymerization temperature; these data are shown in *Figure 4*. At the highest polymerization temperature used in this study, 90°C, the sample crystallinity was found to be ca. 0.35, whereas for samples prepared at 40°C, the sample crystallinity increased to 0.46. Also shown in this figure are the results of Ovenall and Uschold at higher polymerization temperatures (○); there, too, crystallinity was found to be a decreasing function of polymerization temperature.

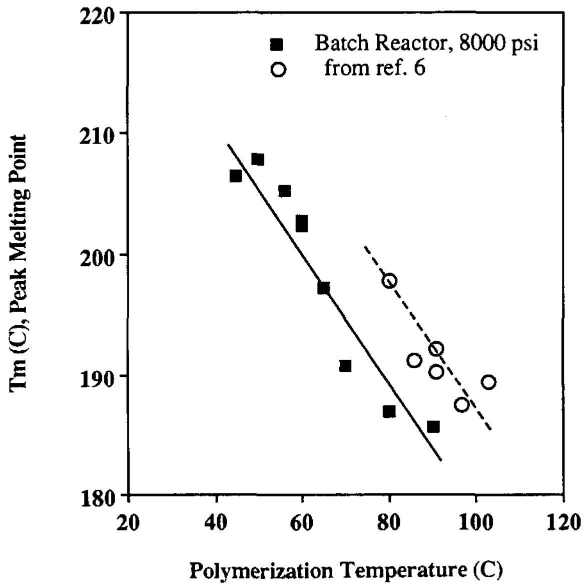

Figure 2 Melting point of PVF *versus* the polymerization temperature used to prepare the polymer. Samples were polymerized at a pressure of 8000 psi (~55 MPa)

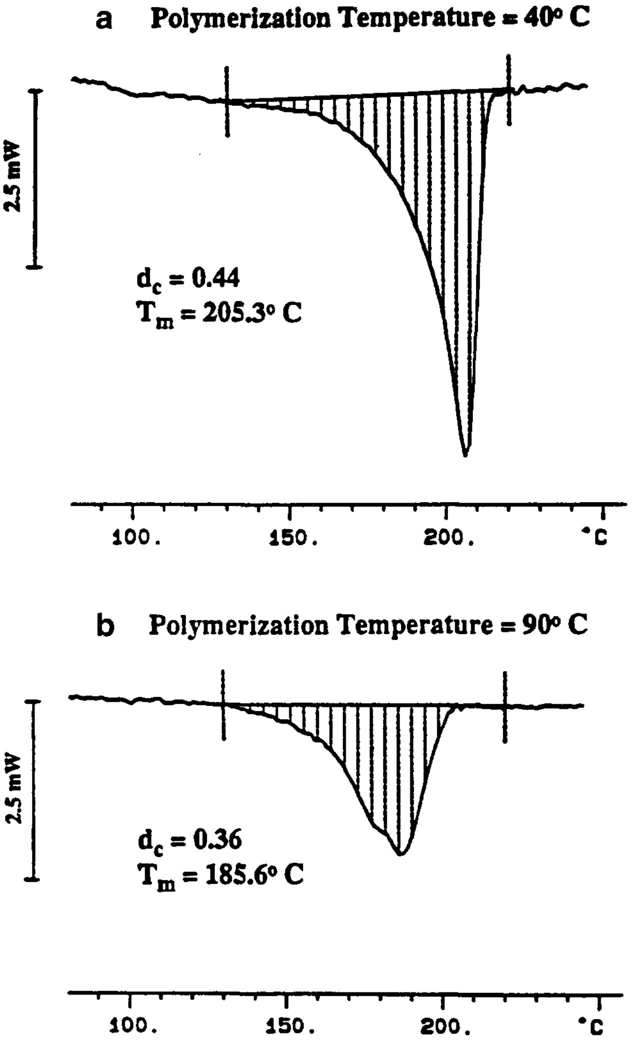

Figure 3 Melting endotherms of PVF prepared at a polymerization temperature of (a) 40°C and (b) 90°C

Polymerization pressure

A series of PVF samples were prepared at polymerization pressures ranging from 900 to 15000 psi (~6.2 to 103 MPa), while maintaining a constant polymerization temperature of 60°C in the batch reactor. These results, summarized in *Figure 5*, demonstrate that, as the polymerization pressure was increased, the polymer melting point was found to remain essentially constant at ca. 202°C. In addition, for samples polymerized at a

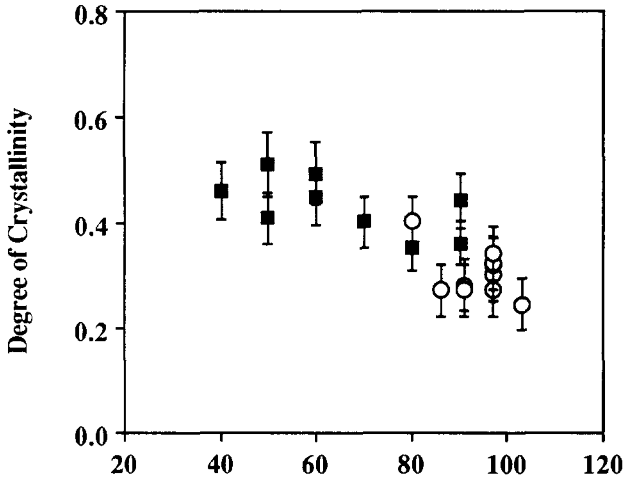

Figure 4 Crystallinity of PVF samples as a function of polymerization temperature used to prepare the polymer

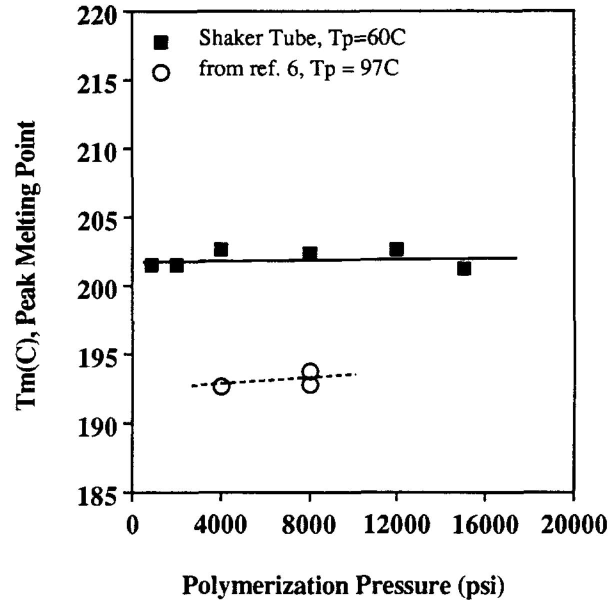

Figure 5 Melting point of PVF *versus* polymerization pressure used to prepare the polymer

higher polymerization temperature of 90°C, we have observed a similar behaviour (data not shown). In that case, too, the melting point remained largely constant with increasing polymerization pressure. Likewise, these results are in good agreement with those obtained for PVF samples produced at a polymerization temperature of 97°C in a large-scale continuous reactor (○). In that study only a negligible dependence of the melting point on polymerization pressure was observed, over the narrow range of pressures studied.

Quantitative analysis of melting endotherms for the samples prepared in the batch reactor at 60°C is summarized in *Figure 6*. It is evident that the degree of crystallinity in the samples, ca. 0.40, was found to be virtually independent of the polymerization pressure. Thus, whereas modifying the polymerization temperature of VF was found to have pronounced effects on the melting characteristics of PVF, varying the polymerization pressure produced only modest changes.

^{19}F n.m.r. analysis

The influence of polymerization conditions in governing the microstructure of PVF, and in turn its melting behaviour, was investigated with ^{19}F n.m.r. analysis. Following the previously adopted convention, the unit –CHF– is arbitrarily designated as a 'head'. Displayed in *Figure 7* is a plot of the frequency of the head-to-head linkages as a function of the polymerization temperature, for polymers prepared at a pressure of 8000 psi (~55 MPa). As indicated, at 40°C the number of head-to-head monomer additions was found to be $12.5 \pm 1.5\%$, or roughly one monomer reversal per eight additions. Moreover, this value was found to increase very slowly with increasing polymerization temperature. This observation is in good quantitative agreement with the results of Ovenall and Uschold[6], whose data are also shown in *Figure 7* (○). From both sets of data, it can be readily concluded that the number of head-to-head units in PVF is only a very weakly increasing function of polymerization temperature. Furthermore, these results are in good agreement with previous n.m.r. analyses of PVFs that were prepared at comparable temperatures[1,2].

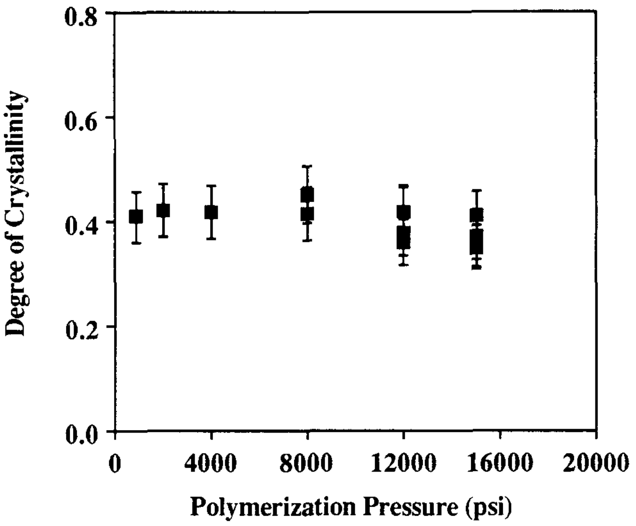

Figure 6 Crystallinity of PVF samples as a function of polymerization pressure used to prepare the polymer. Polymerizations were carried out at 60°C

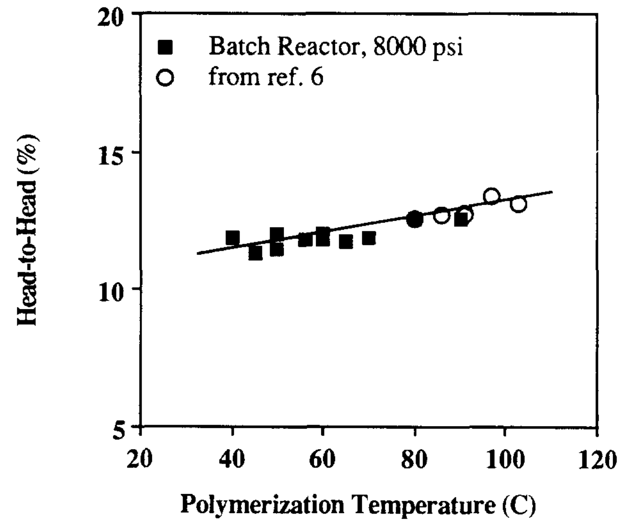

Figure 7 Plot of head-to-head units (%) in PVF as a function of polymerization temperature

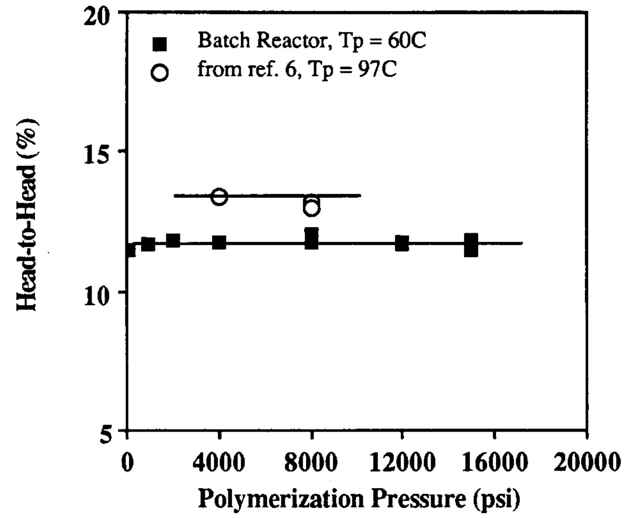

Figure 8 Plot of head-to-head units (%) in PVF as a function of polymerization pressure

The effects of polymerization pressure on the frequency of head-to-head additions is summarized in *Figure 8*, for samples prepared at a temperature of 60°C in the batch reactor (■), and at 97°C in the large-scale continuous reactor (○). Again, it can be seen that for PVFs produced at the higher polymerization temperature the number of head-to-head linkages was slightly higher, i.e. 13.5% vs. ca. 12%; more importantly, however, it is clearly evident that the frequency of head-to-head units was found to be largely invariant with respect to the polymerization pressure.

In contrast to the apparent weak dependence of regio-sequencing on polymerization temperature and pressure, the role of polymerization conditions in governing chain branching can be quite pronounced. Shown in *Figure 9* is a plot of the percentage of chain branch points (associated with tertiary fluorine atoms) in the polymer *versus* the polymerization temperature used*. From this figure it is apparent that decreasing the polymerization temperature substantially decreases the number of chain branch points. Namely, for samples prepared at a polymerization temperature of 90°C, the frequency of chain branch points was found to be 1.35% (or one branch per 75 monomer additions), whereas for polymer prepared at 40°C, chain branching is decreased to 0.3% (i.e. one branch per 300 monomer additions). Similarly, for PVFs prepared at 8000 psi in the continuous reactor (○), it is clear that the amount of chain branching decreased strongly with decreasing polymerization temperature.

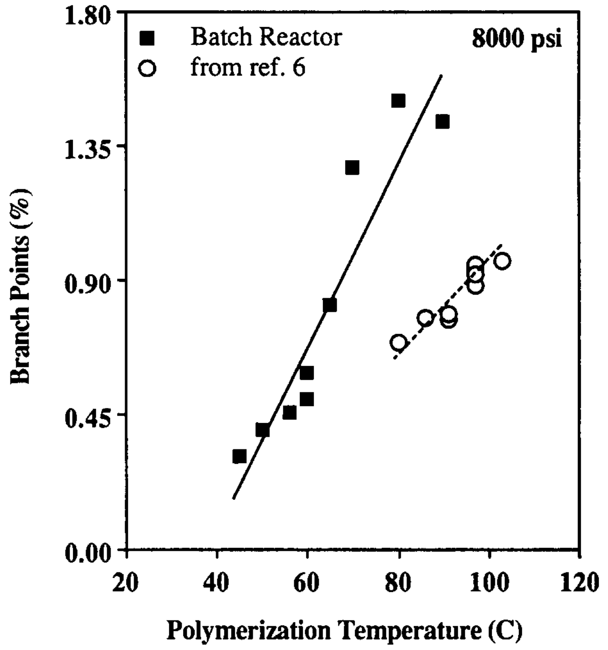

Figure 9 Plot of the percentage of branches in PVF (associated with tertiary fluorine atoms) as a function of polymerization temperature

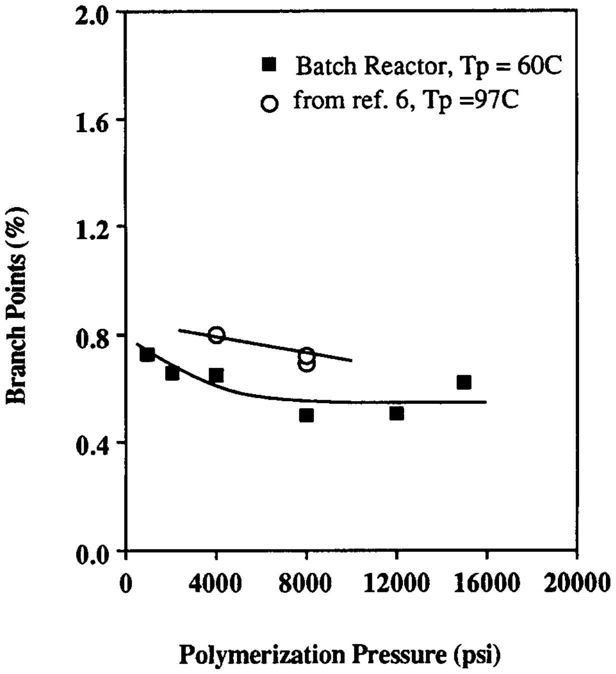

Figure 10 Plot of the percentage of branches in PVF (associated with tertiary fluorine atoms) as a function of polymerization pressure

By comparison, the influence of polymerization pressure on chain branching is modest, as shown in *Figure 10*. These data correspond to PVF samples that were polymerized at 60°C in the batch reactor. We observed that increasing the polymerization pressure from 900 to 8000 psi (~6.2 to 55 MPa) reduced the fraction of branch points from 0.75% to ca. 0.5%, whereas further increases in polymerization pressures produced no apparent change. Also shown in this figure are data for samples polymerized at 97°C in the large-scale continuous reactor. Again, the number of branch points was found to decrease only slowly as the polymerization pressure was raised from 4000 to 8000 psi (~27.6 to 55 MPa).

DISCUSSION

The results presented in this study clearly demonstrate that the melting characteristics of PVF are strongly dependent on polymerization temperature, and only

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*The branch points (%) reported here consist of branches on –CF– units that are attached in either a head-to-head or head-to-tail manner, as illustrated in *Figure 1*. Generally, we find that 20–30% of the branches are associated with a head-to-head linkage. It should also be emphasized that the likely presence of branch points associated with tertiary hydrogen atoms has not been investigated in this study. Hence, the *total* concentration of branch points in the PVF backbone may be considerably higher weakly dependent on polymerization pressure. In particular, decreasing the polymerization temperature from 90 to 40°C was found to increase the peak melting point of PVF by ca. 20°C, whereas increasing the polymerization pressure from 900 to 15 000 psi ($\sim$6.2 to 103 MPa) produced only minor effects on T_m. Moreover, decreasing the polymerization temperature was observed to narrow the breadth of the melting endotherm, and concomitantly to increase the sample crystallinity. In contrast the effects of polymerization pressure on the overall sample crystallinity were found to be modest.

In addition, high-resolution ^{19}F n.m.r. analysis clearly reveals that in our study the observed changes in the melting point of PVF are associated primarily with differences in the number of chain branch points, and not the regio-regularity. That is, *Figures 7–10* show that the pronounced increase in the melting point of PVF, which results from decreasing the polymerization temperature, accompanies a substantial decrease in the number of chain branch points, whereas the frequency of head-to-head linkages remained largely constant. Similarly, the weak dependence in the melting characteristics of PVF with increasing polymerization pressure was found to mirror the relatively small decrease in the number of chain branch points as the pressure was raised; here, too, the number of head-to-head additions was found to remain largely constant. These results strongly suggest that the melting point of PVF is governed by the branch-point content — provided the regio-sequencing remains generally the same — irrespective of the polymerization conditions used to prepare the polymer. Indeed, such an expectation is borne out, as shown in the plot of polymer melting point *versus* branch points, displayed in *Figure 11*. It is apparent that the melting points of the PVF samples prepared in the batch reactor, as well as those in the large-scale continuous process, are well described by a single curve. Namely, for PVF with a branch-point content above 1.4% ($\sim$one branch per 70 monomer additions), the melting point is reduced to ca. 185°C, whereas for samples with branch-point content less than 0.3% ($\sim$one branch per 300 monomer additions), the melting point lies above 206°C.

Still, a further test of the determinant role that branching plays in governing the melting characteristics of PVF can be made by examining the data for a series of PVF samples prepared in a small-scale one-litre continuous reactor. In this case, a range of polymers were prepared by varying the agitator reactor speed from 400 to 1100 rpm while maintaining a constant polymerization temperature and pressure of 97°C and 8000 psi ($\sim$55 MPa) respectively. Varying the agitator speed controls the degree of mixing, the size of the monomer droplets and hence the availability and concentration of VF in the growing PVF particles. In turn, these factors govern the *relative* rates of chain propagation to chain transfer. For example, we reasonably expect that under conditions of poor mixing, only a low concentration of monomer is available during the polymerization, hence favouring the formation of chain branches.

Shown in *Figure 12* is the dependence of polymer melting point on the reactor agitator speed. When the agitator speed was raised from 400 to 900 rpm the melting point of PVF was found to increase steeply from 178 to 193°C, whereas at higher agitator speeds the melting point remained essentially constant. Moreover, as shown in *Figure 13*, this increase in melting point occurs over identically the same magnitude of agitator speeds in which a marked decrease in the concentration of branch points from 2.2 to 0.8% was observed; and here, too, no further change in branch points was observed at speeds above 900 rpm. On the other hand, over the same range of agitator speeds, the head-to-head content was found to *increase* slowly, but steadily, with increasing agitator speed, as shown in *Figure 14*. Clearly such an *increase* in the head-to-head linkages cannot explain the *increase* in the melting point of PVF. Additionally, as shown in *Figure 11*, the data for these PVFs plotted along with the data for samples polymerized in the

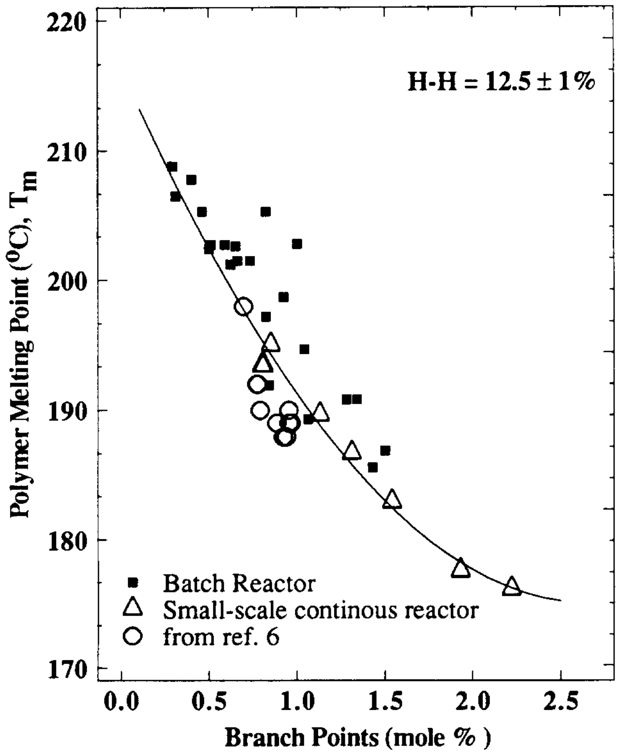

Figure 11 Plot of melting point in PVF *versus* branch points (%) associated with tertiary fluorine atoms

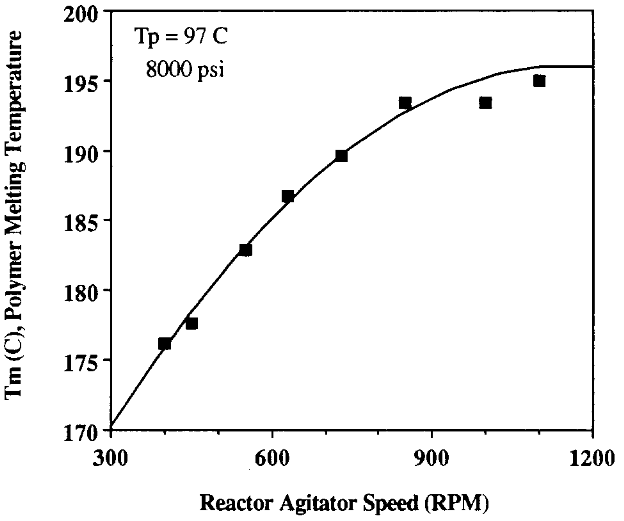

Figure 12 Plot of melting point in PVF *versus* the agitator speed in the small-scale continuous reactor. Samples were polymerized at a temperature of 97°C and a polymerization pressure of 8000 psi ($\sim$55 MPa)

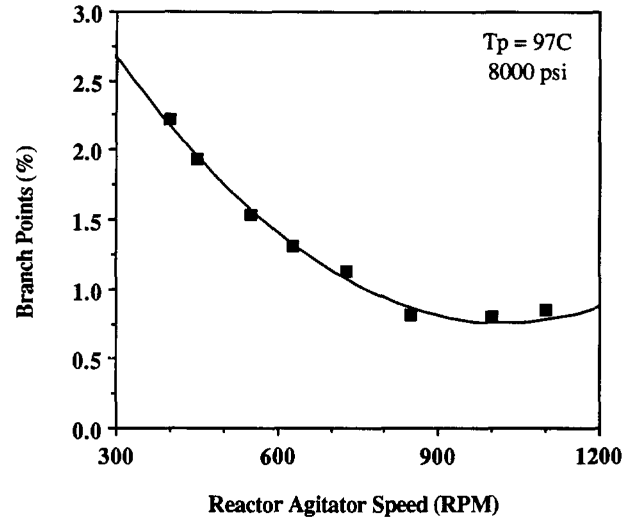

Figure 13 Plot of percentage of branch points in PVF *versus* agitator speed in the small-scale continuous reactor

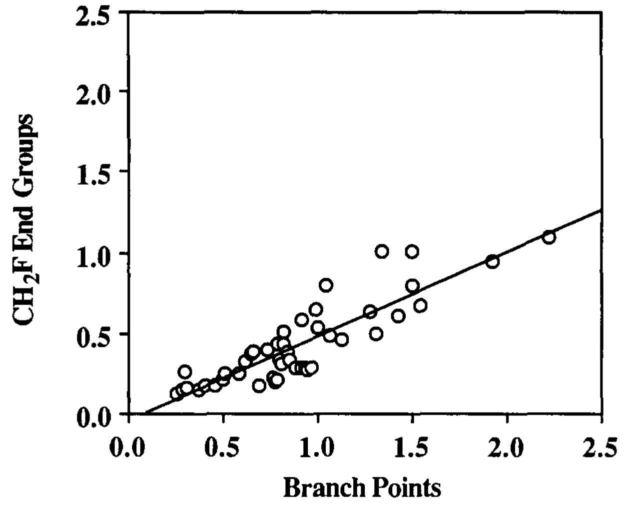

Figure 15 Plot of CH_2F end groups in PVF *versus* tertiary fluorine branch-point content

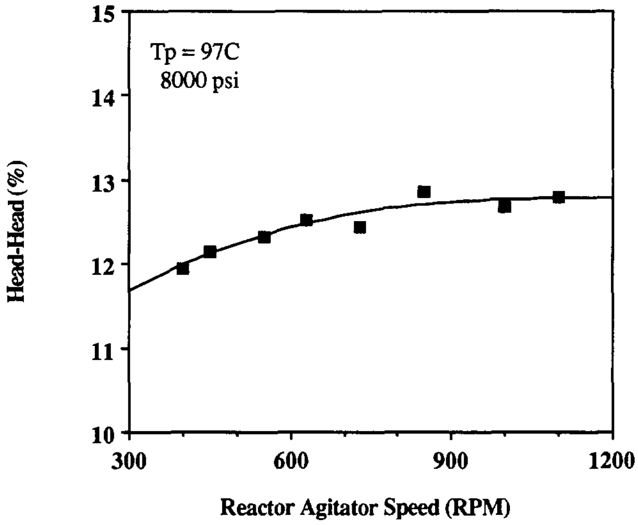

Figure 14 Plot of head-to-head units (%) in PVF as a function of agitator speed in the small-scale continuous reactor

batch reactor and the large-scale continuous reactor further demonstrate that branch-point content largely determines the melting point of PVF. Again, it is worth emphasizing that for all of the data shown in this figure, the percentage of head-to-head linkages was 12.5 ± 1.5%.

The salient results of this study may be contrasted with previous reports of the melting behaviour of PVF in the literature. In a recent study, Cais and Kometani[3] have suggested that the melting point of PVF is solely dominated by the frequency of monomer reversals, and moreover showed that T_m varied by 30°C for samples with largely different regio-regularities. Similarly, Hanes[14] and Lando have ascribed differences in the melting point of PVF to varying extents of regio-ordering in the backbone. While it may be reasonably expected that regio-ordering will influence polymer melting, these workers, however, failed to investigate the important role of chain branching. In view of the synthetic route used to prepare these other PVFs, it seems likely that they too contained branches. Since empirically we find that the number of chain branch points is an increasing function of the head-to-head content, it seems likely that in these other studies, too, chain branching may have been a significant factor in controlling T_m. On the other hand, the results reported here are entirely consistent with those of Ovenall and Uschold[6], who have recently suggested that differences in the concentration of branch points can largely govern the melting characteristics of PVF.

Lastly, we conclude by speculating on the mechanism by which the tertiary fluorine branch points are produced. It seems probable that their formation is the result of a $-CHF^{\cdot}$ radical abstracting a hydrogen atom from a growing chain, concomitantly producing a CH_2F end group[6]. Nevertheless, if this were the only mechanism for forming tertiary fluorine branch points, then the number of CH_2F end groups would be comparable to the branch-point content. However, our ^{19}F n.m.r. analysis clearly demonstrates that, while the percentage of CH_2F end groups is directly proportional to the percentage of tertiary fluorine atoms, as shown in *Figure 15*, in all cases this latter quantity is found to be larger, by roughly a factor of 2. Thus, other reaction mechanisms must also be important. For example, $CH^{\bullet}$ radicals may combine and, in some cases, form chemical crosslinks, or possibly hydrogen abstraction may preferentially occur at a $CH_2^{\bullet}$ radical resulting in methyl-terminated end groups. Which, if either, of these mechanisms is dominant cannot be addressed from our data. Clearly, further studies employing proton n.m.r. may shed light on this mechanism, as well as allow for a quantitative investigation of chain branching associated with tertiary hydrogen atoms.

CONCLUSIONS

We have investigated the effects of chain microstructure on the melting characteristics of PVF. Polymers were prepared over a broad range of polymerization conditions. In general, decreasing the polymerization temperature was found to produce a marked increase in the polymer melting point (T_m), whereas increasing the polymerization pressure produced only minor effects on T_m. As demonstrated by ^{19}F nuclear magnetic resonance analysis, the pronounced increases in T_m can be traced to a substantial decrease in (tertiary fluorine atom) chain branching, whereas for the same polymers the regio-regularity remained largely constant.

ACKNOWLEDGEMENTS

The authors acknowledge important contributions to this study by B. J. Wilson and L. A. Peterson, who assisted in the preparation of the polymers. This study has also benefited from helpful discussions with R. Uschold. The skilled technical assistance of K. P. Leach and W. J. Desmond is also gratefully acknowledged.

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