Solid-State Synthesis and Morphology of Poly(ferrocenyldimethylsilane)

J. Rasburn, R. Petersen, T. Jahr, R. Rulkens, I. Manners,* and G. J. Vancso*,†

*Department of Chemistry, University of Toronto, 80 St. George St.,
Toronto, Ontario M5S 1A1, Canada*

Poly(ferrocenyldimethylsilane) (PFCDMS, **2**) was synthesized by γ-irradiation of the crystalline monomeric [1]ferrocenophane, $Fe(\eta\text{-}C_5H_4)_2SiMe_2$ (**1**), in the solid state. The resulting degree of polymerization showed a dependence on the initiating radiation dose. The morphology of the polymer films obtained by solvent casting was examined and compared with PFCDMS samples made in the thermally induced polymerization of the molten monomer. Wide-angle X-ray diffraction and differential scanning calorimetry indicate a typical crystallite size of 77 Å, a degree of crystallinity of about 50%, and a corresponding enthalpy of fusion of 7 J g⁻¹ (1.9 kJ mol⁻¹) for the as-cast film samples. Additionally, using these analyses, comparison of the polymer obtained by solid-state polymerization with that from melt polymerization shows that the degree of crystallinity following film casting was similar in each case. Optical microscopy revealed numerous, small regions of birefringence. Emanating fibrillar aggregates of width 90 nm were observed by atomic force microscopy. On the basis of the structural characteristics as a whole, the polymer films show a sperulitic morphology.

Introduction

The recently accomplished synthesis of high polymers containing ferrocene moieties in the main chain by ring-opening polymerization methods has sparked a keen interest in these materials.[1] Several years previously, Neuse, Rosenberg, and their respective co-workers had produced low-molecular-weight ferrocene-containing polymers via condensation routes.[2,3] Other studies have involved polymers and oligomers featuring ferrocene both in the main chain and as a side group, thus taking advantage of the presence of iron so as to be able to utilize techniques for structural studies, e.g., Mössbauer spectroscopy,[4,5] which are not often available to polymer scientists. In this way, structural aspects such as the glass–rubber transition have been examined from a different perspective.

The synthesis of high-molecular-weight poly(ferrocenyldimethylsilane) by thermal ring-opening polymerization was first reported in 1992.[6] Subsequent publications have focused on the preparation of a range of analogous poly(ferrocenylsilanes) and the unusual properties of these materials.[7–13] Conspicuous promise

lies in the progression to the preparation of materials as yet unobtainable by other routes, such as novel magnetic materials,[14] and much interest retains in the unusual electrochemical behavior of these polymers.[1,6,9,11–13]

The present study focuses chiefly on morphological aspects of one of the polymers recently synthesized, namely, poly(ferrocenyldimethylsilane) (PFCDMS). In addition to an examination of the polymer prepared by the usual route involving melt polymerization, two features of the cyclic starting monomer have been recognized as advantageous for the purpose of solid-state polymerization involving high-energy radiation as an initiator. The first is that the monomer is strained and polymerizes by ring-opening[6–9] in which case a small dose of γ-radiation should be sufficient to initiate the process. The second is that the monomer is highly crystalline, and this combined with the ring strain offers the possibility of a direct transformation from a monomer crystal to a polymer crystal. It could be envisaged that a higher degree of crystallinity would obtain, resulting either from the retention of a highly crystalline form throughout polymerization generally or by the reduction of branching reactions, for example, if these occur. In this situation, the superior linearity of the polymer obtained in the solid state would be expected

* To whom correspondence should be addressed.
† Present address: University of Twente, Faculty of Chemical Technology, P.O. Box 217, NL. 7500 AE Enschede, The Netherlands.
⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1995.
(1) Manners, I. *Adv. Organomet. Chem.* **1995,** *37,* 131.
(2) Neuse, E. W. *J. Macromol. Sci., Rev. Macromol. Chem.* **1970,** *C4,* 110.
(3) Sheats, J. E.; Carraher, C. E.; Pittman, C. U. *Metal-Containing Polymer Systems;* Plenum: New York, 1985.
(4) Brooks, J. S.; Care, C. M.; Plimley, S. *Hyp. Int.* **1984,** *20,* 151.
(5) Feyerherm, R.; Litterst, F. J.; Burkhardt, V.; Nuyken, O. *Solid State Commun.* **1992,** *82,* 141.
(6) Foucher, D. A.; Tang, B. Z.; Manners, I. *J. Am. Chem. Soc.* **1992,** *114,* 6246.
(7) Finckh, W.; Tang, B.-Z.; Foucher, D. A.; Zamble, D. B.; Ziembinski, R.; Lough, A. J.; Manners, I. *Organometallics* **1993,** *12,* 823.
(8) Foucher, D. A.; Ziembinski, R.; Tang, B.-Z.; Macdonald, P. M.; Massey, J.; Jaeger, C. R.; Vancso, G. J.; Manners, I. *Macromolecules* **1993,** *26,* 2878.

(9) Foucher, D. A.; Ziembinski, R.; Petersen, R.; Pudelski, J.; Edwards, M.; Ni, Y.; Massey, J.; Jaeger, C. R.; Vancso, G. J.; Manners, I. *Macromolecules* **1994,** *27,* 3992.
(10) Tang, B. Z.; Petersen, R.; Foucher, D. A.; Lough, A. J.; Coombs, N.; Sodhi, R.; Manners, I. *J. Chem. Soc., Chem. Commun.* **1993,** 523.
(11) Rulkens, R.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **1994,** *116,* 797.
(12) Nguyen, M. T.; Diaz, A. F.; Dement'ev, V. V.; Pannell, K. H. *Chem. Mater.* **1993,** *5,* 1389.
(13) (a) Manners, I. *J. Inorg. Organomet. Polym.* **1993,** *3,* 185. (b) Foucher, D. A.; Ziembinski, R.; Rulkens, R.; Nelson, J.; Manners, I. *Inorganic and Organometallic Polymers;* Allcock, H. R., Wynne, K., Wisian-Neilson, P., Eds.; *ACS Symp. Ser.,* in press.
(14) Hmyene, M.; Yassar, A.; Escotne, M.; Percheron-Guegan, A.; Garnier, F. *Adv. Mater.* **1994,** *6,* 564.
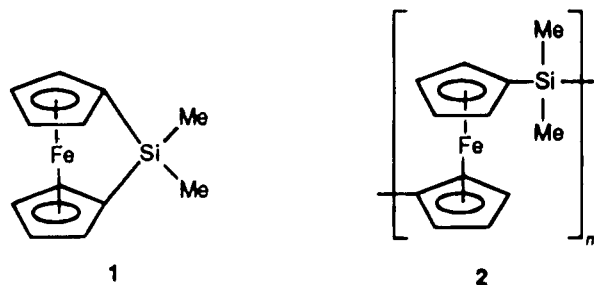
Figure 1. Schematic representations of the [1]ferrocenophane monomer, ferrocenyldimethylsilane, **1**, and poly(ferrocenyl-dimethylsilane), **2**.

to provide more favorable crystallization behavior and kinetics during subsequent processing and recrystallization.[15]

The method of solid-state polymerization originated in the 1930s[16,17] with the generation of poly(oxymethylene) from trioxane. This system was the subject of much interest subsequently.[18-20] Moreover, this reaction is classed as a topotactic process, in that the crystal structure of the product is related to that of the monomer. Notable aspects of the mechanism from a physical point of view include the change in unit-cell dimensions on polymerization and the effect of temperature which, it has been conjectured, may serve to relieve matching difficulties presented by the structural alteration.

To obtain a crystalline polymeric product directly from a crystalline starting material, a resemblance between the crystal structures of each is required. Thus the initiation and propagation may take place without large translations of monomer molecules as these would not be accessible in the crystalline state at temperatures well below melting. Hence the retention of crystallinity implies topotaxis, though this will not be addressed explicitly in this report.

Experimental Section

Synthetic Procedures. The method of preparation of the monomer **1** (Figure 1) and melt-polymerized polymer is that reported previously by Foucher et al.[6] Heating of the monomer (1.0 g, melting point, 78 °C) at 130 °C for 10 min in vacuo produced molten polymer in the first instance and then, following a steady increase in viscosity, a solid substance, confirmed by GPC and ^{1}H NMR analysis to be the polymer, poly(ferrocenyl-dimethylsilane). Following further heating for a period of 30 min, the polymeric product was purified by dissolving in THF (40 mL), concentrating this solution to approximately 10 mL and then precipitating the polymer by adding the solution in THF to an excess (300 mL) of hexanes. The precipitate was filtered, redissolved in toluene, filtered through a membrane of pore size 0.2 μm, concentrated to 10 mL (a solution of

approximately 1%) and then either precipitated in acetone or set as a film. Glass plates were used as surfaces for setting films, and leveling was effected by adjustment of a proprietary mounting for the plates, suitable alignment being indicated by a spirit level. A glass Petri dish was used to cover the solution during drying, which took place over several hours at room temperature. The films were an amber color.

For polymerization in the solid state, the monomer (ca. 0.1 g) was sealed under vacuum in a glass tube and placed in a ^{60}Co γ-ray source at 30 °C. Three dosages were used, 2.5, 5, and 10 Mrad, the dose rate being 0.88 Mrad/h. It was observed that on completion of a given irradiation, the temperature of the enclosure chamber was never more than 38 °C, and therefore safely below the melting range of the monomer. On removal from the γ-ray source, the sealed tube was transferred to an oven and held at 60 °C for 6 h. Purification and processing of the polymeric product followed the method described above for the case of melt polymerization. However, it was found that there was a significant amount of insoluble material, and the exact nature of this is as yet unclear. Percentage yields by weight of polymeric product, not inclusive of insoluble material, were approximately 20% after a dosage of 2.5 Mrad, 40% after 5 Mrad, and 50% for 10 Mrad. It is noteworthy, however, that following an irradiation at the highest dose, 10 Mrad, subsequent omission of the heat treatment had no affect on the yield compared to the case where this heat treatment was included.

Instrumental Procedures. Gel permeation chromatography (GPC) was carried out on a Waters Associates instrument incorporating a Model 510 HPLC pump and 410 differential refractometer. Molecular weights are specified using polystyrene standards for column calibration.

X-ray diffraction maxima were obtained at room temperature (25 °C) on a Siemens D5000 diffractometer which incorporated a solid-state detector tuned for Cu Kα_1 radiation (λ = 1.5406 Å), thus circumventing the problem of iron fluorescence.[21] Scanning was carried out using the method of monitoring the scattered radiation at discrete increments of scattering angle, the latter ranging from 2 to 40°. The step size was 0.05° (of 2θ), and the collection time per step was 35.0 s. Film samples were used in all cases and examined in transmission geometry. The goniometer moved in a vertical arc around the sample mounting, i.e., a meridional scanning geometry was used. No correction was made for the polarization of the scattered beam.[22] Throughout a given scan, the film was rotated such that the angular velocity swept out by the normal to the plane of the film relative to the original straight-through direction (2θ = 0°) was half that of the detector ($\omega-2\omega$) in order to maintain constancy of scattering volume. The scattering profiles were fitted with either Voigt or Pearson functions, these in turn being convolutions of Lorentzian and Gaussian profiles.

Thermal analysis by DSC were carried out on film specimens using a Perkin-Elmer Series 7 instrument in the range 0–430 °C and at a heating rate of 10 °C min^{-1}.

(15) Mandelkern, L. *Crystallization of Polymers*; McGraw-Hill: New York, 1963; pp 265ff.

(16) Schultz, J. *Polymer Materials Science*; Prentice-Hall Inc.: New Jersey, 1975; Section 2.12.

(17) Thakur, M. Solid State Polymerisation. In *Encyclopaedia of Polymer Science and Engineering*; Kroschwitz, J. I., Ed.; John Wiley & Sons: New York, 1989; Vol. 15.

(18) Chatani, Y.; Uchida, T.; Tadokoro, H.; Hayashi, K.; Nishi, M.; Okamura, S. *J. Macromol. Sci.: Phys.* **1968**, *B2*, 567.

(19) Wunderlich, B. *Adv. Polym. Sci.* **1968**, *5*, 568.

(20) Andrews, E. H.; Martin, G. E. *J. Mater. Sci.* **1973**, *8*, 1315.

(21) Alexander, L. E. *X-ray Diffraction Methods in Polymer Science*; Wiley-Interscience: New York, 1969.

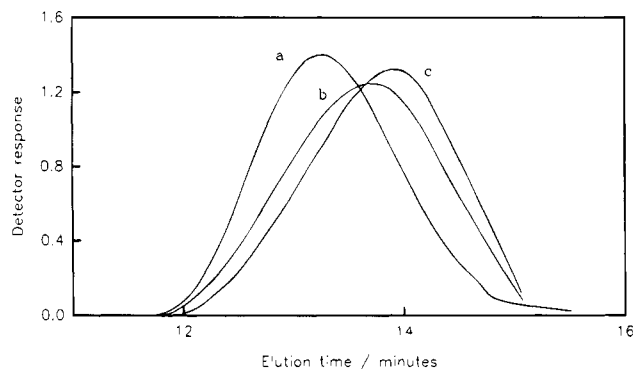(22) Baltá-Calleja, F. J.; Vonk. C. G. *X-ray Scattering of Synthetic Polymers*; Elsevier: Amsterdam, 1989.

Figure 2. GPC traces of 1% solutions in THF of poly-(dimethylferrocenylsilane): (a) melt-polymerized polymer, (b) polymerized using 10 Mrad initiating dosage, and (c) 2.5 Mrad initiating dosage.

Optical examination was undertaken on an Olympus BH-2 metallurgical microscope in both transmission, using circularly polarized light, and reflection. For variable-temperature examination, a Mettler FP80 HT hot plate was used with a slightly different set of objective lenses, these having a longer working distance.

Atomic force images were obtained using a NanoScope III (Digital Instruments) in Tapping Mode and with a D-scan head, Silicon NanoProbe cantilever and scan rate of 2 Hz.

Results and Discussion

Elution times from GPC analysis for melt- and solid-state-polymerized material (2.5 and 10 Mrad irradiation) are shown in Figure 2. There appears to be a slight dependence of molecular weight on radiation dose; a higher dose produces a greater value of the weight average molar mass, M_w, indicating a greater extent of polymerization (M_w = 220 kDa for the 2.5 Mrad sample and 260 kDa for the 10 Mrad sample). There is also a slightly greater polydispersity at the higher dose. This may indicate that the solid-state polymerization method provides a means of controlling of the molecular weight. However, the differences in molecular weight in this instance are small, and at this early stage their origin is uncertain. For example, it is arguable that branching occurs resulting from cross-linking subsequent to cleavage of the C−H bond of the methyl group.

The higher yield can be understood on the basis of a larger number of reaction centers produced with higher dose, and these in turn would be distributed more thoroughly among the crystals of the specimen.

Comparing the molecular weights of the solid-state polymerized material with that of the melt-polymerized polymer determined previously,[8] it can be seen that with 10 Mrad the molecular weight of the former approaches (M_w = 260 kDa, M_w/M_n = 1.5) that of the latter (M_w = 330 kDa, M_w/M_n = 1.4), though with a slightly greater dispersity involved.

X-ray diffraction maxima of melt- and solid-state polymerized (10 Mrad) poly(ferrocenyldimethylsilane) (PFCDMS) are shown in Figure 3, and an example of the resolution of one of these in terms of its component contributions is shown in Figure 4. There are two points to note. First, concerning the scattering behavior in general, the most obvious feature is the large peak at 13.90° (2θ), indicating an interplanar spacing of 6.3

Å, in agreement with both our previous findings[13] and those of Nguyen et al.[12] In contrast to the latter workers, however, it can be seen that there is a notable amorphous content in the present case, which, bearing in mind the similarity of synthesis at least as far as the melt-polymerized polymer is concerned, may stem from differences in processing subsequent to synthesis.

Second, the data of Figure 4 lends itself to an estimation of crystallite size and degree of crystallinity. In the first instance, one may assume for simplicity perfect crystals and a sharp demarcation between ordered, crystalline regions and disordered, amorphous regions, in which case a lower bound for size and content is obtained. The full width at half-maximum height of the main peak in Figures 3 and 4 suggests a crystallite size of 77 Å according to the Scherrer equation, namely

$$L_{hkl} = [(2 \cos \theta/\lambda)\delta\theta]^{-1}$$

where L_{hkl} is the average length dimension of the crystallite in the [hkl] direction, $\delta\theta$ the full width at half-maximum height (in radians), λ the wavelength of the X-radiation used, and θ the Bragg angle for this reflection (2θ = 13.90° in this case).

For the degree of crystallinity, taking peak numbers 1, 4, and 6 in Figure 4 as crystalline and the others as amorphous, a value of roughly 48% is obtained. The basis of these assignments is peak width: it is noticed for peaks 1, 4, and 6, $\delta\theta \leq 10^{-2}$ rad, for 3 and 7, $\delta\theta \approx 1.3 \times 10^{-2}$ rad, and for 2 and 5, $\delta\theta > 2 \times 10^{-2}$ rad. Hence, peaks 1, 4, and 6 appear to be consistently narrower than the others and attributable to crystalline reflections. Peaks 2, 3, and 5 comprise collectively the main amorphous halo and should not be taken as necessarily representing distinct individual structures. This calculation has tacitly assumed the same scattering power for both crystalline and amorphous phases. In general, this is not the case because the density and hence the electron density is not distributed homogeneously throughout the material[21] for a "two-phase" polymer, but reasons why it is felt that this does not constitute such a severe approximation in the case of this polymer will be ventured shortly in connection with the melting behavior. Overall, then, it may be concluded that although the crystallites are somewhat small, they are present in significant proportion.

It was mentioned above that the values of the crystallite size and degree of crystallinity are conservative estimates. If paracrystallinity was taken into account,[21,22] though even for the second kind two well-resolved orders are required, the crystallite size would be found to be significantly larger (since it would no longer be the only source of line broadening) and the intensity for a given scattering interval would have to be readjusted, so that the estimated degree of crystallinity would be larger.

With regard to the distinction between PFCDMS obtained by melt polymerization and that produced in the solid state, it can be seen that there is very little difference. X-ray diffraction traces (a) and (b) in Figure 3 have not been normalized in any way but arise from a fortuitous similarity in sample thickness. Also shown in Figure 3 is a specimen of PFCDMS polymerized in the solid state but with a smaller dose (2.5 Mrad). It needs to be added that this is also a thinner specimen but, this accepted, it appears to give a broader main
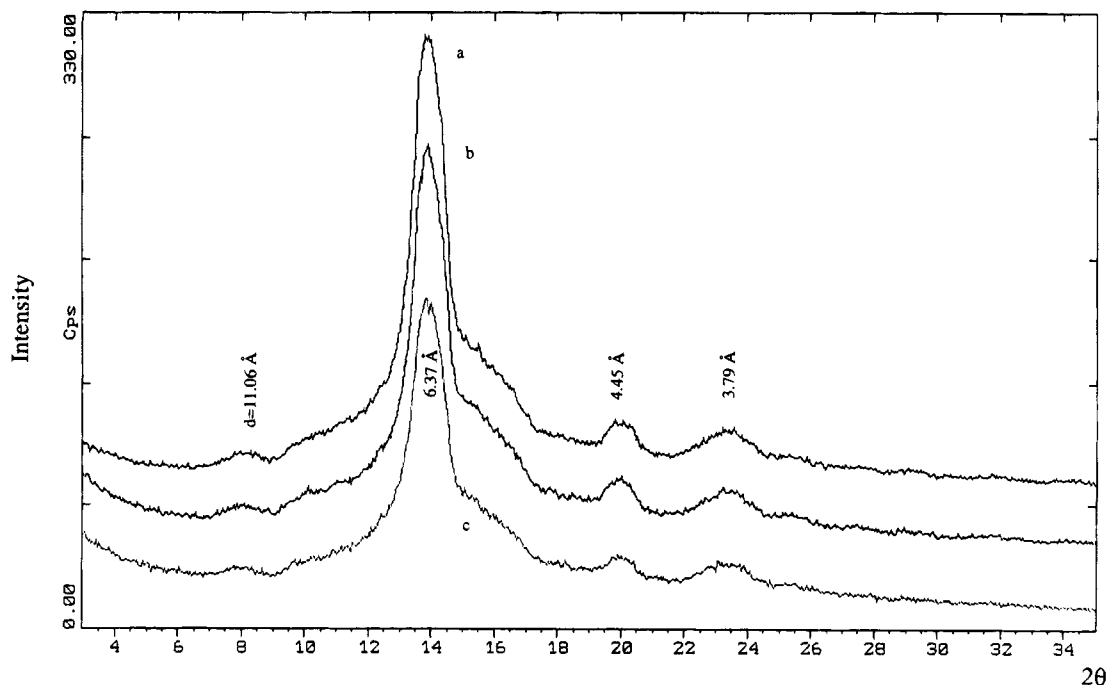
Figure 3. Wide-angle X-ray diffraction profiles of three types of PDMFCS: (a) 10 Mrad solid-state polymerization; (b) melt polymerization; (c) 2.5 Mrad solid-state polymerization.
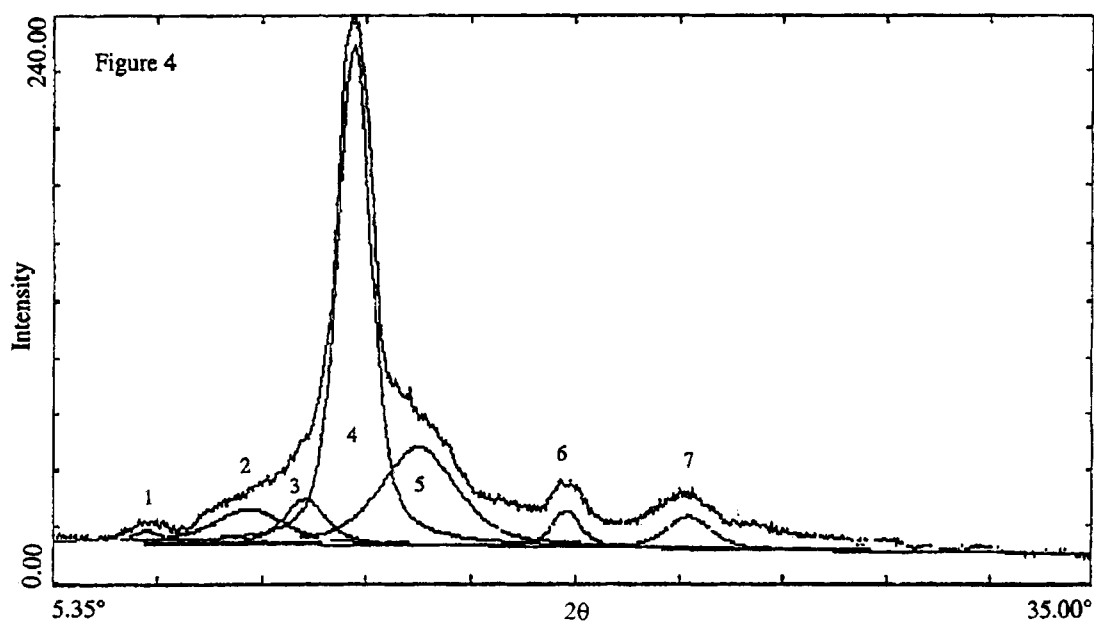

Figure 4. Resolution of the X-ray profiles from the 10 Mrad sample in terms of its constituent maxima using Voigt profiles.

peak. Were it to be assumed that this indicates a smaller crystallite size and is not simply an artifact of the sample dimensions and also bearing in mind the results of GPC (Figure 2), it could then be conjectured that the molecular weight of the polymer has a more cogent effect on the crystallite size rather than any radiation damage that may have been incurred.

It is worth noting at this juncture the crystal structures of the oligo(ferrocenyldimethylsilanes) synthesized by Rulkens et al.[11] using an anionic initiation method. A plausible notion may be that the WAXS profile of the polymer forms an envelope around that of the pentamer (Figure 5). The weaker, i.e., more attenuated, reflections in the pattern of the pentamer would be lost, owing to a greater distortion of the structure in general, and these would then be indistinguishable from the amorphous scattering. For instance, some adjustment of

position and intensity for reflections nearer the periphery of the scattering interval may occur in going from the pentamer structure to that of the semicrystalline polymer. This may be understood by observing that in the case of the pentamer the ferrocenyl groups at the ends of the chain are (a) oriented at right angles to the plane bisecting vertically the interior units, and (b) closer to the neighboring ferrocenyl groups (5.66 Å between the iron atoms involved) than the three interior ferrocene units are to each other (6.91 Å Fe—Fe distance). This orientation of the ferrocenyl groups could not be accommodated in the crystal structure of the polymer, so that other reflections associated with this orientation would not arise.

The main diffraction peak in Figures 3, 4, and 5a is much more intense than other features in the pattern, and it seems reasonable to ascribe it to the distance
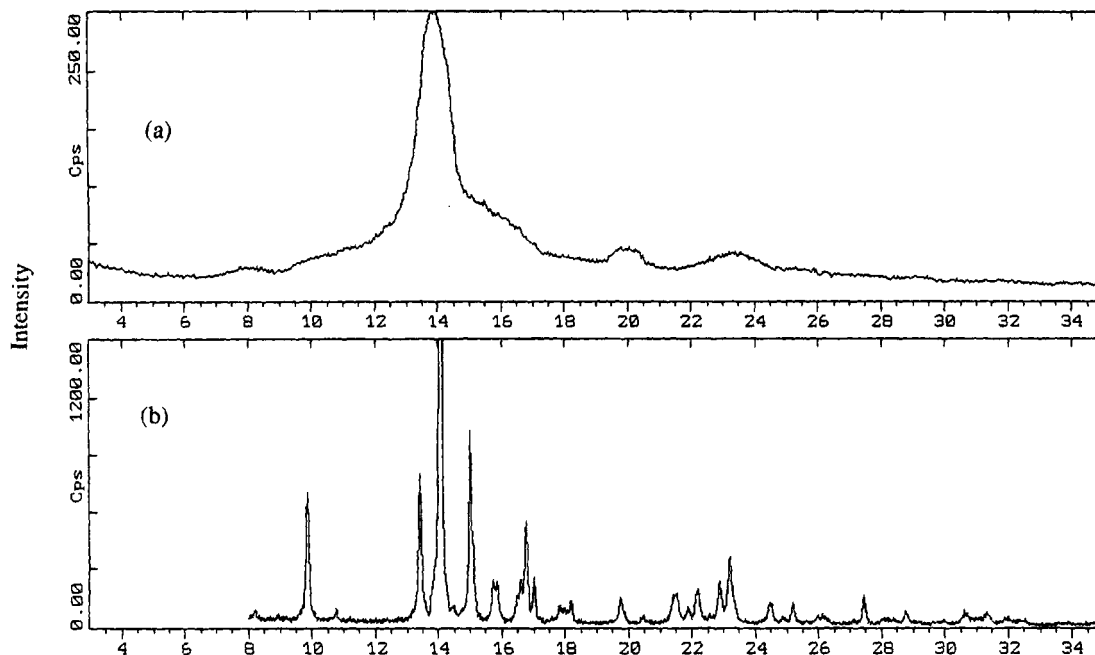
Figure 5. Comparison of X-ray profiles for (a) the 10 Mrad sample and (b) pentamer obtained by anionic initiation (see ref 11).
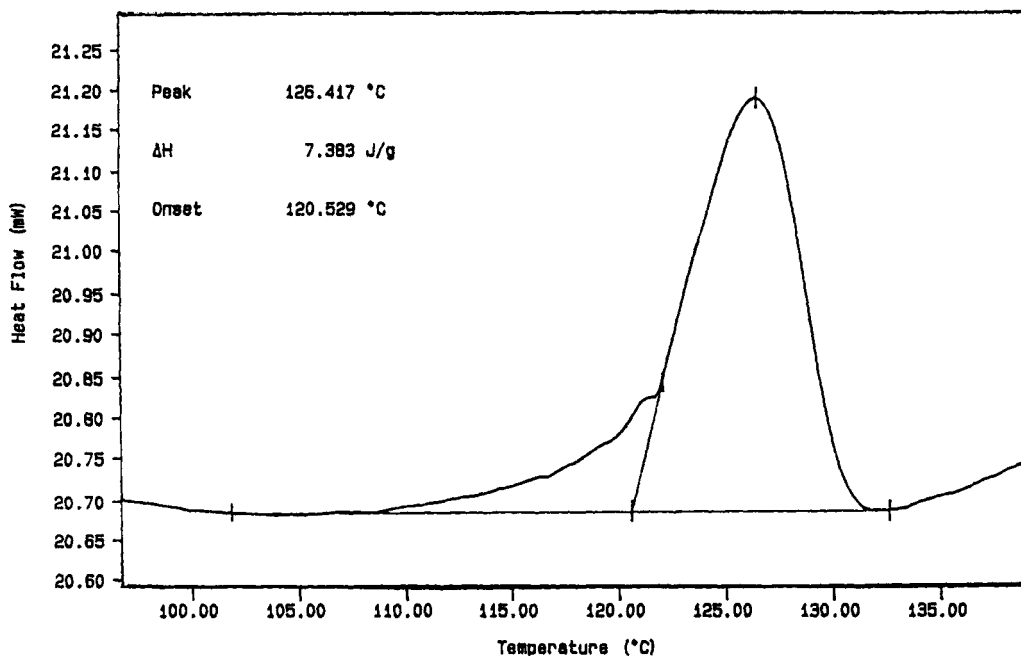

Figure 6. DSC melting endotherm at 10 °C min^{-1} of the solid-state (10 Mrad) polymerized sample.

between planes containing iron, as this element has a much greater electron density, and hence scattering power, than the other elements in the chemical structure. However, bearing in mind the results obtained previously for the pentamer crystals as mentioned above, it seems unlikely that it corresponds to a straightforward c axis repeat distance in the trans conformation in the polymer. In fact, for the pentamer crystals, this main peak has been attributed to the (011) planes.[23]

The latent heats of melting (ΔH_m) determined by DSC are found to be the same within experimental error for all three samples, and a conventional form of endotherm is found in each case, a typical example being illustrated in Figure 6. It is notable that ΔH_m is also quite small at 7 J g^{-1}. Bearing in mind that the degree of crystallinity is approximately 50% and assuming that the amorphous regions of the polymer do not contribute to the measured endotherm, this implies a value of 14 J g^{-1} for a sample of 100% crystallinity, or 4 kJ/mol of monomer unit. This value is very much smaller than a highly ordered polymer such as polyethylene ($\Delta H_m \approx$ 290 J g^{-1},[24] or 8 kJ mol^{-1}, for the equilibrium crystal) and is more in the region of the cellulosic materials ($\Delta H_m \approx$ 12–30 J g^{-1} (4–12 kJ mol^{-1})[24]). Such a low

(23) This assignment is evident in the additional information available with ref 11. The determined $d_{(011)}$ is 6.282 Å.
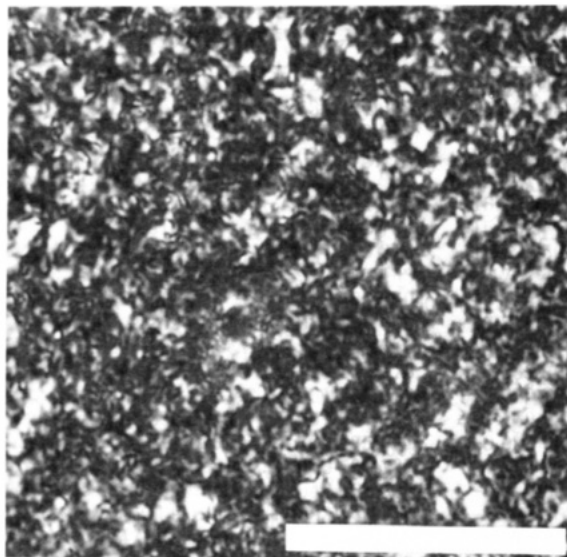
(24) In ref 15, pp 119ff.

Figure 7. Transmission optical micrograph, magnification 1000×; scale bar indicates 50 μm.

value for ΔH_m may suggest that the packing in the crystalline phase is not much better than in the amorphous regions, and so their respective densities are similar.

An intriguing finding with this material is that after melting and then cooling at a range of cooling rates (2–200 °C min^{-1}), the melting endotherm at 120 °C did not recur during a second, identical heating regime, i.e., irreversible melting occurs in the strictest sense of the term. A reasonable explanation may be that this absence arises from a kinetic effect owing to steric hindrance, such that in the molten phase and in the time scale of cooling (a maximum of 75 min between 200 and 50 °C), there is insufficient freedom and independence of molecular motion to return to an ordered phase, whereas such movements are possible in solution and given a drying time of several hours, as used for the preparation or films. Going by their respective glass transition temperatures, it is likely that the inclusion of the ferrocene moiety imparts a certain rigidity to the main chain in comparison with the corresponding polysilanes.[1,8] Such a chain stiffness may be sufficient to hamper chain folding during melt crystallization or inhibit chain folding altogether, so that a morphology reminiscent of the fringed micelle may pertain.

Optical micrographs in circularly polarized light at a magnification of 1000 are presented in Figure 7. In transmission mode using crossed polars, it can be seen that there are small regions of birefringence but little in the way of a discernible overall form on a larger scale. Small, black, extinction lines are visible and may be attributable to a jumbled assembly of different crystallite orientations which may be expected as a consequence of crystallization far from equilibrium. There does not appear to be any clear sightings of disclination points of the type observed when smectic or nematic phases are present;[25] moreover, no change in the arrangement of these lines is observed as the temperature is taken through the melting range. The disappearance of birefringence at 130 °C (the maximum temperature

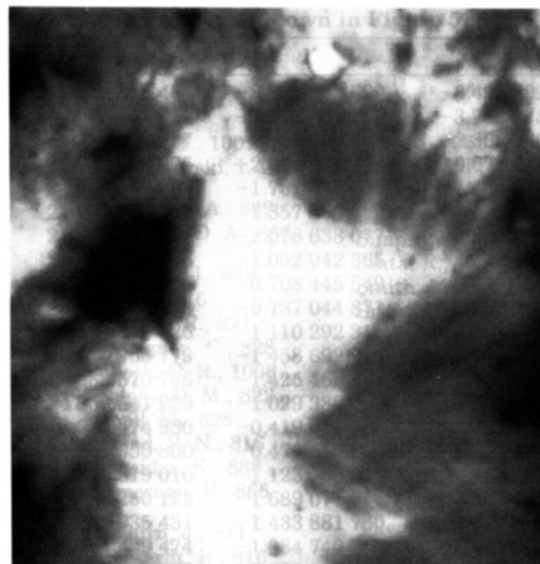**Figure 8.** Atomic force micrographs of 2.5 Mrad solid-state polymerized poly(dimethylferrocenylsilane): (a, top) scan area 5 μm × 5 μm; (b, bottom) scan area 0.7 μm × 0.7 μm.

of the DSC melting endotherm) when the sample was heated at 10 °C min^{-1} confirmed this transition to be the final clearing temperature.

The morphology of the film surfaces at high magnification was studied by atomic force microscopy (AFM). The images of the 2.5 Mrad solid-state polymerized sample are shown in Figure 8, where Figure 8a corresponds to a 5 μm × 5 μm scan, and Figure 8b to 0.7 μm × 0.70 μm. The shading on these micrographs is proportional to the height of the features with dark areas being the lowest and bright areas being the highest points. The presence of radiating features with typical size of a few micrometers is confirmed by AFM.

The radiating features captured at very high magnification can be seen in Figure 8b. These can be identified as twisted fibrillar structures with typical widths of approximately 90 nm. Thus the microstructure observed is consistent with a spherulitic morphology in which spherulites are made of radial fibrils

(25) Donald, A. M.; Windle, A. H. *Liquid Crystalline Polymers*; Cambridge University Press: Cambridge, UK, 1992.

arranged in a radial pattern. The fibrils consist most probably of crystallites of ordered polymer.

Evidently from the small size of the crystallites suggested by the X-ray diffraction maxima and the low value for the enthalpy of fusion, the crystalline phase at room temperature of this polymer is not greatly different in terms of order from its disordered phase. However, this polymer remains a solid at temperatures above its glass transition temperature, so it is unlikely that it could be classed as liquid crystalline, plastic crystalline, or either of the respective glasses within these categories.[26] A more comprehensive examination of the structure, thermal properties, and chain dynamics would enable an accurate classification of the crystalline phase of this material, and detailed studies of the higher, symmetrically substituted homologues in such a study may assist in this respect.

Conclusions

It has been found that polymerization of the silicon-bridged [1]ferrocenophane, **1**, can be accomplished in the solid state, and that this method also provides a means of controlling the extent of polymerization. Wide-angle X-ray diffraction indicates that there is a substantial crystalline content but that the crystallites are small. The low latent heat of fusion suggests a considerably disordered crystal. Atomic force microscopy reveals the presence of spherulitic structures in which the constituent, radiating fibrils are also evident.

CM940464U

(26) Wunderlich, B.; Möller, H.; Grebowicz, J.; Baur, H. *Adv. Polym. Sci.* **1988**, *87*.