

The effect of cooling rate upon the morphology of quenched melts of isotactic polypropylenes

P. J. Hendra, J. Vile, H. A. Willis and V. Zichy

Department of Chemistry, The University, Southampton, SO9 5NH, UK

and M. E. A. Cudby

ICI Petrochemical & Plastics Division, Welwyn Garden City, Herts, UK

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Experimental data are provided on the molecular structure of paracrystalline samples of quenched melts (glasses). We propose that rods of helical molecules are present in the 'glasses', their length being sensitive to the temperature of the melt from which the 'glass' is produced, the amount of time held in the melt and the rate of quenching.

A comparison is made between samples crystallized from the melt and those crystallized via the glassy phase. By measuring the lamellar thickness, from Raman spectroscopy, and calculating the absorbance ratio A_{998}/A_{973} from infra-red spectroscopy, longer helical sequences were shown to exist to a greater extent in the samples crystallized from the melt. Samples crystallized from the glassy phase contained shorter helical sequences.

In investigating the effect of the surrounding temperature on solid polypropylenes, we have shown that the density of the material can be related to the temperature of storage. We comment on the relevance of this observation to dimensional stability in mouldings.

(Keywords: isotactic polypropylene; glassy state; crystallinity; infra-red absorption; helical sequences; moulding conditions)

INTRODUCTION

Isotactic polypropylene is capable of crystallizing into a variety of modifications by slowly cooling the melt¹⁻³. Rapid quench cooling produces a phase of low order variously described as a glass or as a smectic phase⁴. Warming the latter to temperatures near 80°C results in crystallization to α crystalline form.

Although there is little debate regarding the structure of the crystallized phases, considerable discussion, largely unresolved, has occurred on the precise nature of the glass or smectic* phase. In an earlier paper⁵ we investigated the kinetics of crystallization of the glass *versus* the melt, commented on the significance of the order and made some suggestions on the structure of the various phases involved. In this paper we broaden the investigation to include the structure of the glass and the subtleties in the structure of the semicrystalline material produced by warming the glass. A variety of experimental methods have been used and are described below.

EXPERIMENTAL

The isotactic polypropylene used in this investigation had a tactic purity of 98% from ¹³C n.m.r. data and molecular weight characteristics $M_n = 77\ 000$, $M_w = 567\ 000$.

For much of the experimentation, thin-film specimens of glassy material were required. In order that these are

suitable for study by infra-red absorption the thickness of the film has to be less than 80 μm and of good constancy across the specimen, and the film has to be free from voids. To achieve these ends in a violently quenched melt specimen is experimentally demanding but was achieved as follows. Thin-film specimens were prepared by compression moulding of pellets between heated platens on a hot press. The films were then sandwiched between aluminium foils in which windows 5 \times 10 mm were cut, i.e. the foils in effect acted as a support for a small free area of film in their centre. The sandwiches were then suspended in an oven at various temperatures for approximately 2 min (careful checking using small thermocouples showed that \sim 50 s was required for the sample to warm to the oven's temperature) before being plunged vigorously into liquid nitrogen. To maximize the cooling rate the latter was contained in a Dewar vessel inside the oven. Alternatively the heated sandwich of polypropylene and aluminium was allowed to cool slowly either by reducing the oven temperature or, where more rapid cooling was required, by removal of the sandwich from the oven into the room environment.

Confirmation that quench cooling specimens had produced a glassy structure was derived from X-ray diffraction (see *Figure 1a*).

As mentioned above, much of the experimental data on the nature of the thin-film specimen was obtained from infra-red absorption. Infra-red spectra were recorded at liquid-nitrogen and room temperatures using several different infra-red spectrometers fitted with a RIIC vari-

* In this paper we will describe the quenched solid material as the glassy phase

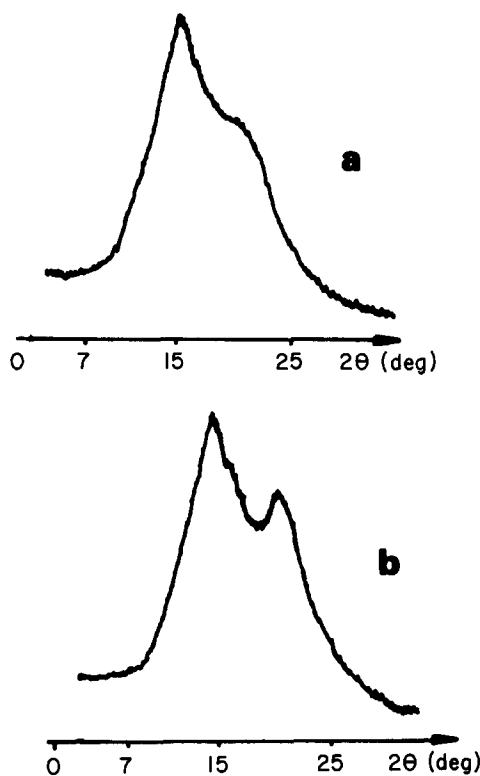


Figure 1 (a) X-ray diffractogram of quenched isotactic polypropylene at liquid-nitrogen temperature. (b) X-ray diffractogram of quenched isotactic polypropylene warmed to room temperature

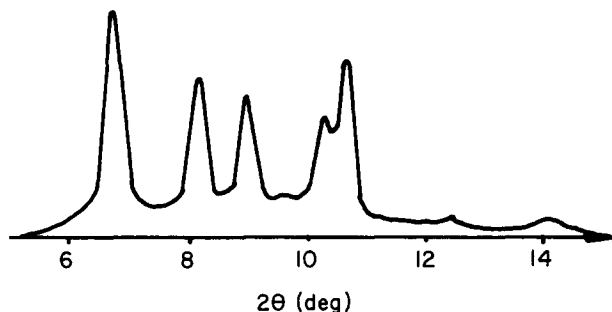


Figure 2 X-ray diffractogram of isotactic polypropylene crystallized from the melt

able temperature sample cell. Spectra were plotted in absorbance and then deconvoluted and integrated on a Dupont curve resolver.

Film thickness has a two-fold influence on the results produced; the cooling rate of a melt curtain is dependent upon its thickness (even if its lateral dimensions are held constant from sample to sample) and the infra-red absorbance varies with thickness. The effect of film thickness was investigated varying the value between 40 and 80 μm . The data expressed arbitrarily as an absorbance ratio of two bands show that considerable changes in property occur when thickness is reduced in the quenched sample held and examined at -190°C . Warmed samples do not show this effect (see *Figure 3a*). Interpretation of the results using methods described below indicate that thicker samples are not completely glassy in structure. Thermal bulk is sufficient in thick specimens to allow some crystallization to occur.

Some Raman spectra were recorded on our polypropylene film specimens. They were recorded on a Coderg

T800 spectrometer powered by a Spectra Physics 170 ion laser operating at 514.5 nm. Density measurements where required were made using a standard density gradient column filled with an ethanol/water mixture.

Analysis of infra-red absorbance data

Many investigations have been reported where attempts have been made to relate the intensity of infra-red absorption bands to the state of order of isotactic polypropylene. Thus the bands at 1220, 1168, 998, 900, 841 and 809 cm^{-1} have at various times been associated with regularity in structure⁶⁻¹⁶ (whether this be due to isolated helices or crystalline zones) whilst those at 1460, 1256, 1171 and 973⁷⁻¹⁶ have been associated with molecules in disordered arrays. As a consequence, 'regularity' has been estimated using infra-red absorption from absorbance ratios, e.g. Luongo⁸ has associated the absorbance ratio A_{998}/A_{973} with helical regularity.

Several authors have attempted to ascribe particular 'regularity' bands to specific structures. Thus, for example, the band at 998 cm^{-1} is thought to arise from regular 3_1 helices ~ 10 monomer units^{7,11,15,17} in extent whereas the band at 841 cm^{-1} arises from somewhat larger sequences¹⁵. The features at 1220, 900 and 809 cm^{-1} possibly arise from extended sequences of regular isotactic polypropylene molecules in helical sequences.

In this report, only the absorbance ratio A_{998}/A_{973} is used as an indication of order. This has been chosen because the two bands lie close together yet are reasonably well resolved and the assignment of their origin is well documented.

The relationship between the absorbance ratio and the molar content of species of interest is poorly documented in the literature because the molecular *irregularity* of standard samples used in the past has been open to doubt. We will air this matter elsewhere but confine ourselves here to expressing the absorbance ratios only, making no attempt to express the molar concentration.

RESULTS AND DISCUSSION

In studies on melt quenching and subsequent rapid crystallization of polyethylene we showed that the solid phase structure was related to the temperature of the precursor melt T_p but that the gradient is slight²¹. In *Figure 3b*, using A_{998}/A_{973} absorbance ratio, we show a remarkable sensitivity in the case of polypropylene but only in samples in the glassy phase which have been kept and studied at cryogenic temperatures.* Warming the specimens to room temperature (i.e. $T_g + 40^\circ\text{C}$) destroys the effect.

Consideration of *Figure 3b* and *Table 1* shows further that:

- (1) little change occurs in any of the specimens with time at constant temperature and
- (2) warming a sample to room temperature whatever its prehistory has a profound effect on its morphology—however, the state of order is not that of the α crystalline form produced by conventional melt crystallization.

Clearly, X-ray diffraction should indicate something of these effects. A sample of quenched polypropylene was

* There is no prospect that this effect could arise from the thermal energy content and its influence on cooling rate. Had this been the dominant issue then $\partial/\partial T_p(A_{998}/A_{973})$ would have been positive

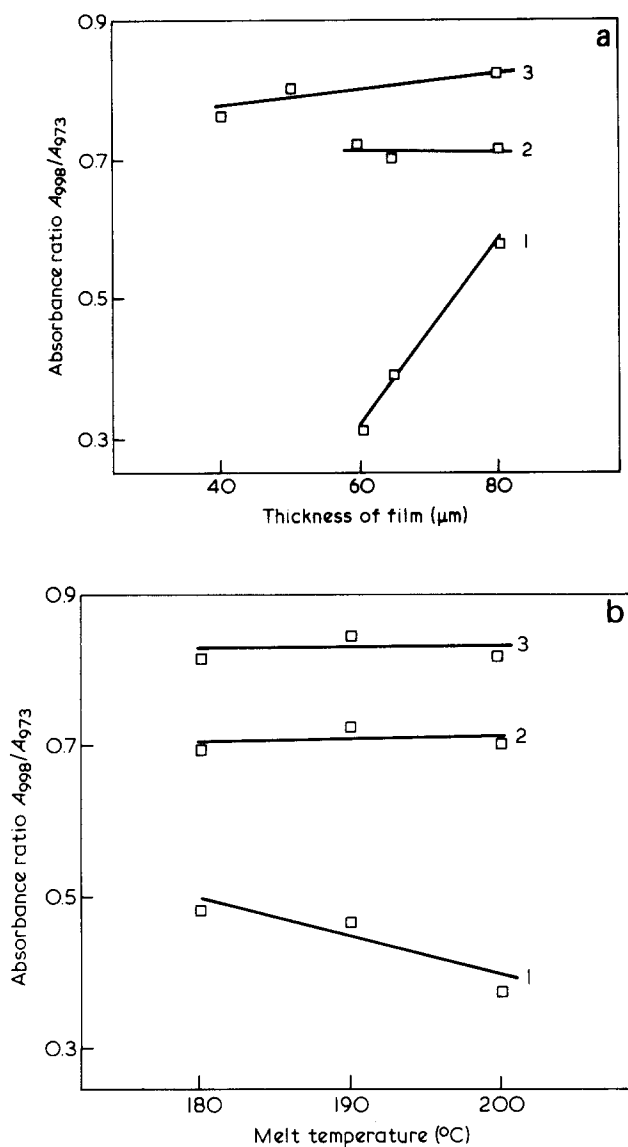


Figure 3 (a) Ratios of absorbances of two infra-red bands for three types of film specimens of polypropylene of thickness T . In experiment 1 the samples were quench cooled from the melt, left at -190°C and examined at that temperature. In experiment 2 the samples from experiment 1 were warmed to room temperature and examined. In experiment 3 the samples were cooled slowly from the melt to room temperature and studied. Error blocks were derived as follows: thickness is variable within $\pm 2 \mu\text{m}$; absorbance ratio error ± 0.02 ; temperature error $\pm 1^{\circ}\text{C}$. (b) Ratios of absorbances of two infra-red bands for three types of film specimens of polypropylene quenched or cooled slowly from various melt temperatures

Table 1 Integrated areas of infra-red absorbance ratio A_{998}/A_{973} of isotactic polypropylene which has been quenched into liquid nitrogen and warmed to room temperature or cooled slowly to room temperature from the melt

Precursor melt temp. ($^{\circ}\text{C}$)	Thermal history		
	Quenched in liq. N_2 Held at -190°C for	then	Cooled down to 25°C
200	0.40 \pm 0.02 after 20 min		0.67 \pm 0.02 after 6 h
	0.39 after 60 min		0.70 after 21 day
190	0.48 after 20 min		0.69 after 6 h
	0.48 after 60 min		0.73 after 21 day
180	0.49 after 20 min		0.70 after 6 h
	0.49 after 60 min		0.71 after 21 day

maintained near -190°C and introduced into a low-temperature X-ray camera. The diffractogram was recorded and is shown in *Figure 1a*. The specimen was then allowed to warm to room temperature and the diffractogram was re-recorded (see *Figure 1b*). (*Figure 2* shows the X-ray diffractogram of melt crystallized isotactic polypropylene.)

It is clear that:

- (1) The degree of order of the quenched cold specimen is very low indeed.
- (2) Warming to room temperature has little effect although slight ordering may be in evidence.
- (3) The quenched sample examined at room temperature is by no means the same as a specimen of the crystalline polymer.

In a previous paper⁵ we have made the latter point and expanded it to show that raising the sample to 80°C or above caused the glassy sample to develop the diffractogram characteristic of α crystallinity. In 1978 McAllister¹⁸, however, showed from careful analysis of the X-ray diffractogram of the glassy material examined at room temperature, that quite considerable local order could be observed in the specimen. Thus we must presume that the glass as originally produced at -190°C is random, that local ordering occurs when it is raised to room temperature and that this expands in extent on subsequent heating to temperatures near 80°C .

Assuming polypropylene behaves in the manner typical of most polymers one would expect the ordering of the glass to occur at temperatures a little above T_g ; its rate of ordering increasing rapidly with temperature. The absorption spectra (between 900 and 1100 cm^{-1}) of polypropylene warmed from -20°C to room temperature are shown in *Figure 4*. In *Figure 5* we present the absorbance ratio A_{998}/A_{973} versus temperature. It can be seen from *Figure 5* that the increase in absorbance ratio A_{998}/A_{973} occurs at T_g .

Turning now to the Raman evidence: in *Figure 6* we present low-frequency Raman spectra of isotactic polypropylene crystallized directly from the melt compared with the glassy material held at room temperature.

The melt crystallized material differs from the glass in that one band near 12 cm^{-1} is produced in the former, bands near 12 and 16 cm^{-1} in the latter. The Raman bands observed are associated with acoustic vibrations of extended sequences of 3_1 helical molecules. Considerable doubt exists, particularly in the case of helical molecules such as polypropylene regarding the equation of the frequency of the acoustic vibrations and the length of the

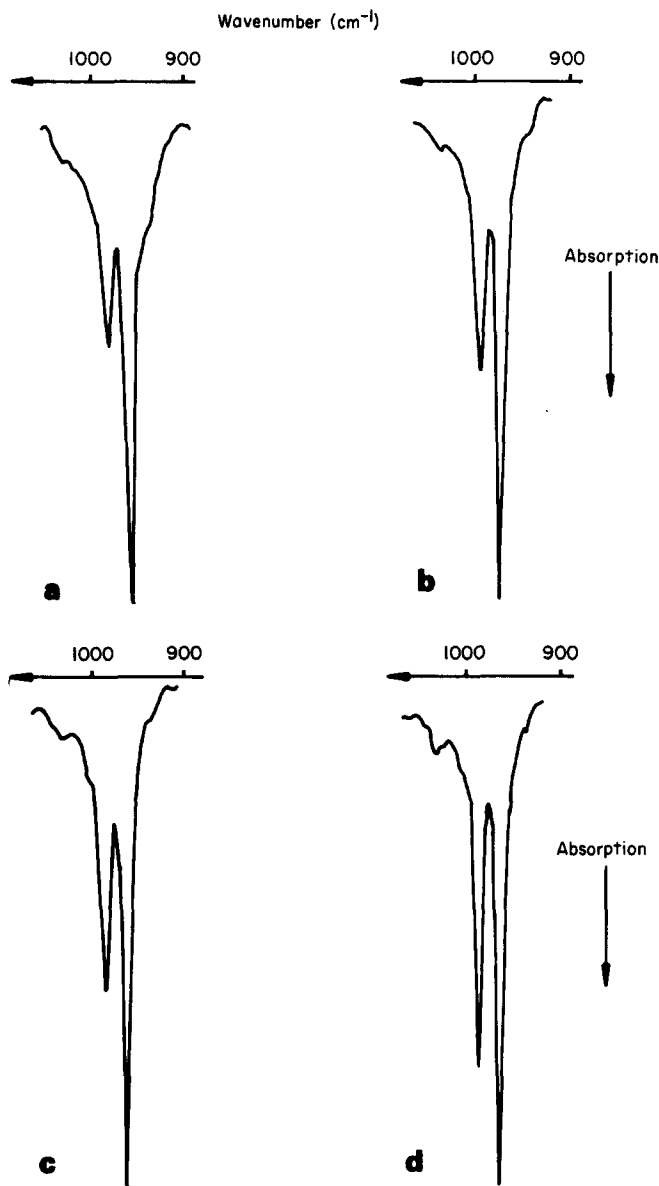


Figure 4 Infra-red absorption spectra of quenched isotactic polypropylene at (a) liquid-nitrogen temperature, (b) -190°C , (c) 0°C and (d) 20°C

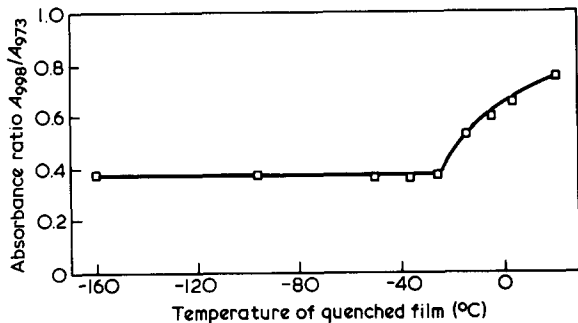


Figure 5 Ratios of absorbances of two infra-red bands of quenched polypropylene that was warmed to room temperature from -160°C . Error blocks were derived as follows: temperature is variable within $\pm 1^{\circ}\text{C}$; absorbance ratio error ± 0.02

extended sequences L . It is, however, clear that the relation between ν and L is inverse. Thus it would appear from Figure 6 that the glass contains species not unlike those in melt crystallized material plus a weak band associated with species of shorter helical sequences.

We must emphasize however that structural factors associated with acoustic vibrations are considerably longer than those 'found' by infra-red absorption ratios and hence may or may not be related to them.

In our earlier paper⁵ we reported on the changes that occur when glassy polypropylene is warmed to various temperatures (up to 100°C) for short periods. The density, X-ray crystallinity and vibrational spectra all alter in a manner suggesting crystallization or order development. We decided here to investigate the matter further with particular reference to the effect of long periods of time.

In Table 2 we report on the effect of surrounding temperatures on the glassy polymer where the environment has been held constant for 4 weeks. Quite clearly

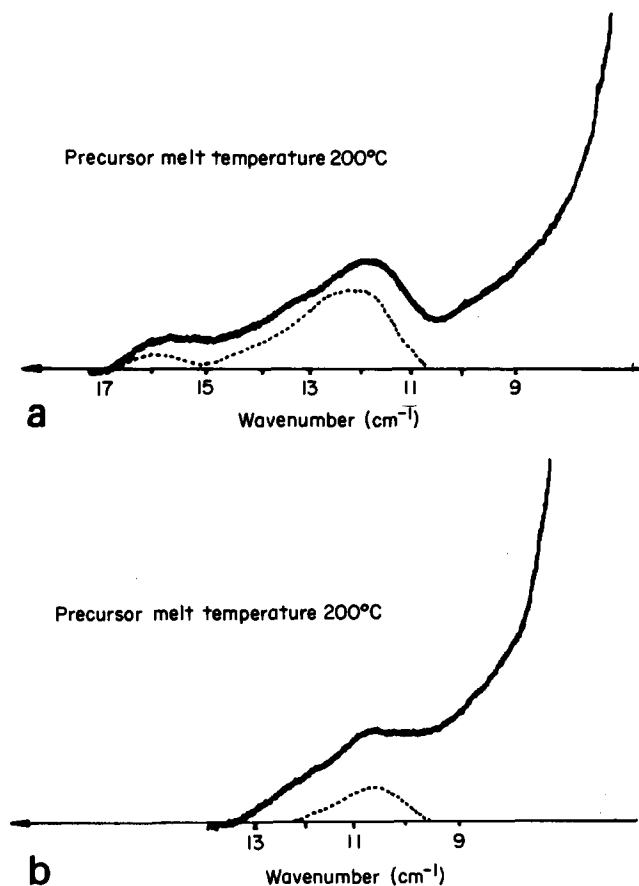


Figure 6 Low-frequency Raman spectra (recorded at room temperature) of polypropylene which had been either (a) quenched into liquid nitrogen or (b) cooled slowly from the melt to room temperature. The deconvoluted LA modes are given underneath each Raman spectrum

Table 2 All samples were quenched into liquid nitrogen and warmed to the surrounding temperatures and held at these temperatures for 4 weeks. State of order of glassy specimens of isotactic polypropylene

Temperature of surroundings ($^{\circ}\text{C}$)	Density (g cm^{-3})	Crystallinity* by density (%)	Absorbance ratio, A_{998}/A_{973}
25 ± 1	0.885 ± 0.003	52 ± 2	0.72 ± 0.02
40	0.889	57	0.76
65	0.892	61	0.80
80	0.898	68	0.85

* Assumes a two-component system with $P_{\text{cryst}} = 0.936 \text{ g cm}^{-3}$ (ref. 19) and $P_{\text{non-cryst}} = 0.85 \text{ g cm}^{-3}$ (ref. 20)

equilibrium has been established during this time, yet it is clear that the order developed stops at a degree which is itself temperature sensitive. This point is emphasized in Figure 7 where it will be seen that the order rapidly approaches asymptotically a plateau value (within 6 h) dependent upon temperature, i.e. a specimen of isotactic polypropylene heated from the glass to a particular temperature for a prolonged period is in a state of metastable equilibrium.

Clearly these observations could depend on the method of production of the glass. In Table 3 we demonstrate that this is not the case. Specimens produced by quenching into liquid nitrogen or ice and water behave identically. This observation has a fascinating consequence in polymer technology. If a specimen of solid polypropylene has been produced under rapid cooling conditions, whether this be by extrusion or moulding (and rapid cooling is, of course, commercially essential) the skin of the product may well be glassy in nature, while the core of a bulky specimen will have crystallized from the melt conventionally. The temperature to which the specimen is warmed in service will then affect the density—the higher the temperature, the higher the density. This change will not occur in the crystalline core material (see Table 3). The consequence must be that bulk specimens

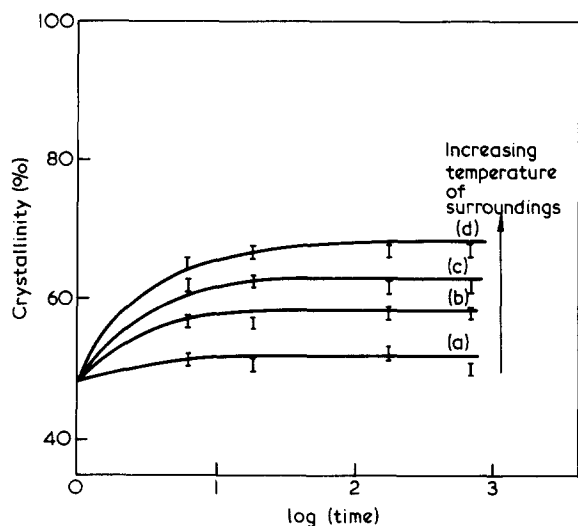


Figure 7 Crystallinity measurements (calculated from the density) of quenched isotactic polypropylene. The samples were held for a period of time at temperatures (a) 25°C, (b) 40°C, (c) 65°C and (d) 80°C

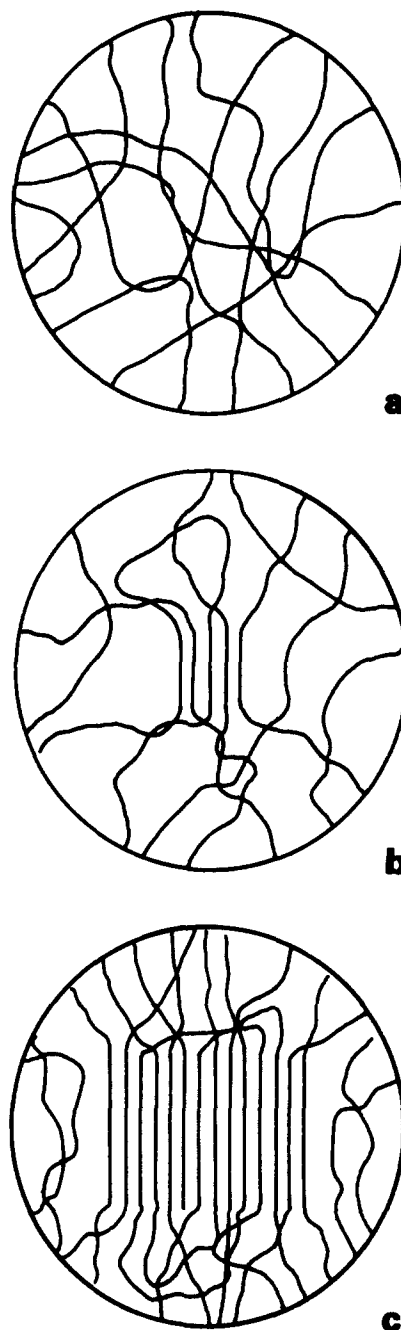


Figure 8 Proposed model for isotactic polypropylene (a) in melt, (b) in the glassy state at low temperature and (c) at temperatures above room temperature

Table 3 All samples had precursor melt temperatures of 180°C and were held at the indicated temperature for 1 week prior to cooling to room temperature before examination

Thermal history	Density (g cm ⁻³)	Crystallinity* by density (%)	Absorbance ratio, A ₉₉₈ /A ₉₇₃
Quenched into liquid nitrogen Held for 1 week at room temp. then Sample was warmed to 65°C	0.887 ± 0.003 0.892	55 ± 2 61	0.75 ± 0.02 0.83
Quenched in iced water and warmed to 25°C Quenched in iced water and warmed to 65°C	0.885 0.892	52 61	0.73 0.84
Slowly cooled to 80°C Slowly cooled to 65°C Slowly cooled to 25°C then warmed to 65°C	0.897 0.904 0.904	67 74 74	0.87 0.87 0.84

* Assumes a two-component system with $P_{\text{cryst}} = 0.936 \text{ g cm}^{-3}$ (ref. 19), and $P_{\text{non-cryst}} = 0.85 \text{ g cm}^{-3}$ (ref. 20) for polypropylene

warmed to high temperatures at any time during service will have skins under tension.

If we assume the density of an unheated glass at room temperature is 0.885 but that after heating to 80°C the value has risen to 0.898 the change must cause a linear contraction of about 0.5%. This places the skin of a bulk specimen under a small permanent tensile stress which must produce a propensity to crack.

In conclusion, we have commented upon the development of order in polypropylene glasses giving experimental evidence on its development as temperature is raised. It is traditional to propose a structural model in this type of work and we indulge by speculating that that shown in Figure 8 would fit our observations.

The suggestion of a fringed micelle morphology is not revolutionary²². The development of order from the glass must take place within a relatively immobile matrix of randomly entangled molecular species. Thus the increase in lamellar thickness that we have observed seems inherently more probably as a result of local conformational change, rather than the large-scale molecular motion that would be necessary if a chain folded model were invoked. Its development must therefore place surrounding molecules under a complex force field at the molecular level. Increasing temperature reduces thermal barriers and permits more crystallization but again leaves the system under stress within the disordered material.

Finally we feel our observation regarding the skin of polypropylene specimens may be of value in explaining some of the stress cracking behaviour or form instability of this polymer in service. We are currently exploring this further and attempting to ascertain what other polymers, if any, show similar effects.

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REFERENCES

- 1 Natta, G. and Corradini, P. *Nuovo Cimento* 1960, **15**, 40
- 2 Keith, H. D. and Padden, F. J. *J. Appl. Phys.* 1959, **30**, 1485
- 3 Turner-Jones, A., Aizlewood, J. H. and Beckett, D. R. *Makromol. Chem.* 1964, **75**, 134
- 4 Natta, G. *SPE Journal* 1959, May, 377
- 5 Glotin, M., Rahalkar, R. R., Hendra, P. J., Cudby, M. E. A. and Willis, H. A. *Polymer* 1981, **22**, 731
- 6 Miyazawa, T. *J. Polym. Sci. Polym. Lett. Edn.* 1964, **2**, 847
- 7 Zerbi, G., Gussoni, M. and Ciampelli, F. *Spectrochim. Acta* 1967, **23A**, 301
- 8 Luongo, J. P. *J. Appl. Polym. Sci.* 1960, **3**, 302
- 9 Kissin, Y. V., Tsvetkova, I. and Cherlov, N. M. *Vysokomol. Soyed.* 1968, **A10**, No. 5, 1092
- 10 Kotschina, A. and Grell, M. *J. Polym. Sci.* 1968, **C16**, 3731
- 11 Miyamoto, T. and Inagakis, H. *J. Polym. Sci. A-2* 1969, **7**, 963
- 12 Heinen, W. *J. Polym. Sci., Polym. Lett. Edn.* 1969, **38**, 545
- 13 Brader, J. J. *J. Appl. Polym. Sci.* 1960, **3**, 370
- 14 Sibilia, J. P. and Wincklehofer, R. C. *J. Appl. Polym. Sci.* 1962, **6**, 556
- 15 Kissin, Y. V. and Rishina, L. A. *Eur. Polym. J.* 1976, **12**, 757
- 16 Samuels, R. J. *J. Polym. Sci.* 1965, **A3**, 1741
- 17 Kobayashi, M., Akita, K. and Tadokoro, H. *Makromol. Chem.* 1968, **118**, 324
- 18 McAllister, P. B., Carter, T. J. and Hinde, R. M. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 49
- 19 Natta, G. and Corradini, P. *Nuovo Cimento Suppl.* 1960, **15**, 40
- 20 'Polymer Handbook', Vol. 23, Wiley, New York, 1975
- 21 Aitken, D., Glotin, M., Hendra, P. J., Jobic, H. and Marsden, E. J. *J. Polym. Sci., Polym. Lett. Edn.* 1976, **14**, 619
- 22 Tadokoro, H. 'Structure of Crystalline Polymers', Wiley, Toronto, 1979, p. 3