Investigation of inter- and intra-molecular packing in the solid state for crystals of normal alkanes and homologous mixtures using FT–IR spectroscopy

G. P. HASTIE, K. J. ROBERTS*
*Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, UK, * and also SERC Daresbury Laboratory, Warrington WA4 4AD, UK*

Fourier transform–infrared spectroscopy has been used to detect conformational defects in certain crystalline n-alkanes ($20 \leqslant n \leqslant 50$) and homologous mixtures. The results indicate the existence of gauche conformers (*trans*-gauche, double gauche and "king") in the low-temperature solid-state structures of the single n-alkanes ($\geqslant n\text{-}C_{36}H_{68}$) and homologous mixtures; implying the existence of end-chain bending and folding. The data have been rationalized in terms of a model which incorporates surface melting and near-neighbour inter-molecular interactions.

1. Introduction

Because aliphatic hydrocarbon chains are a basic component of macro-molecular systems such as lipids [1] and polyethylene [2], short chain n-alkanes, owing to their simplicity, are often used as simple representative models for probing the physical nature of the more complex systems.

In the solid state, the n-alkanes (C_nH_{2n+2}) in general adopt three structurally distinct groups [3]; triclinic $\{12 < n(\text{even}) < 26\}$, orthorhombic $\{n(\text{even}) \geqslant 36$ and $n(\text{odd})\}$ and monoclinic $\{28 < n(\text{even}) \leqslant 36\}$. These materials crystallize in the form of thin plates with regular faces in which the chain direction is more or less perpendicular to the lamellar surface.

Prior to melting n-alkanes are known to exhibit solid–solid phase transitions to crystalline "rotator" phases [4, 5]. In the low-temperature phase (phase I) the chains adopt the overall *trans* configuration, after which the material may transform to a rotator phase (phase II) in which the chains undergo hindered rotation about the main carbon axis. Such a transformation can be accompanied by an introduction of gauche bonds into an otherwise all *trans* structure (see Fig. 1a) with each set of gauche bonds conferring different types of structural disorder, notably:

(i) end gauche (gt) defects: end chain twisting (Fig. 1b)
(ii) double gauche (gg) defects: chain folding (Fig. 1c)
(iii) "kink" (gtg') defects: kinks (Fig. 1d).

Such molecular disorders, which have been previously identified spectroscopically [6–9], are innate to crystals of polyethylene [10] as well as being present in the longer ($n > 100$) chain linear hydrocarbons [11, 12]. In these materials the thickness of the lamellae tends to be less than the average length of the fully extended chain; thus for the chains to pack effectively

within the confines of the lamellae, chain folding is likely. In the case of a single long alkane, the length of the folded chain is an integer fraction of the fully extended chain length; thus the fold and the chain ends must align along the lamellar surface. As a result, end gauche and double gauche conformers (twists and folds) are found at the lamellar surface and thus affect the interlamellar packing, effectively creating an amorphous inter-lamellar region separating the crystalline parts (see Fig. 2).

Ultrasonic methods [13] and a combination of spectroscopic techniques [14–23] (Raman, Fourier transform–infrared, nuclear magnetic resonance), have been previously applied to study such effects from which we now know that

(i) in phase I for $n < 25$, no conformational disorders have been identified. The alkanes of slightly longer chain length, however, possess end-gauche defects in very small concentrations at temperatures just below the transition to phase II;

(ii) in phase II, end-gauche, double gauche and "kink" conformers have been identified in all the alkanes studied.

Spectroscopic studies have also been carried out on the binary system [24, 25] $n\text{-}C_{19}/n\text{-}C_{21}$ which have identified the existence of end-chain disorders in the low-temperature phase.

The "kink-block" theory postulated by Blasenbrey and Pechhold [26] accounts for the presence of gauche conformers in the high-temperature (phase II) solid-state structure of the single n-alkanes. In this phase the chains undergo hindered rotation about the long chain axis; conformational isomers result from a discontinuity in rotation along a section of chain.

The existence of gauche conformers in the low-temperature (phase I) phase ($> n\text{-}C_{25}$) at a temper-

ature just below that of the transition phase II, can be explained in a similar manner if one assumes the change from phase I to phase II is a gradual one; then, as the transition temperature is neared, the intermolecular forces between the chains will weaken. As a result, one or two of the chains may undergo, a number of times, a rotation of 180° accompanied by a translation along the carbon axis resulting in displaced methylene groups at the lamellar surface. As the interchain packing would not be disrupted by such a process, the stable phase I structure would be maintained. The displaced group will be in a thermodynamically less stable environment and will try and re-enter the more stable crystal lattice by either merging with an adjacent crystal (interchain mixing) or by attempting to twist back into the close-packed lattice; thus leading to gauche conformers, as illustrated in
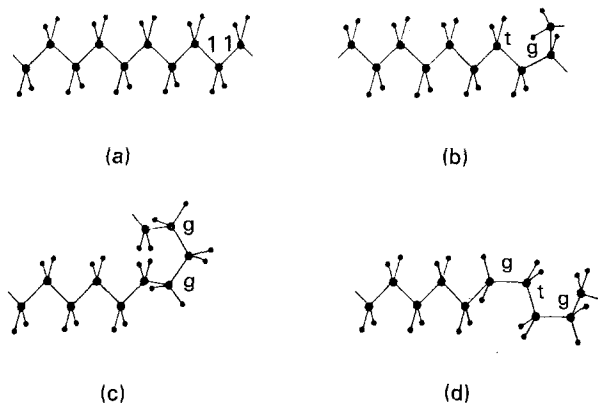

Figure 1 Schematic representation of the possible structural configurations the n-alkane chain can adopt; (a) all-trans, (b) trans-gauche (tg), (c) double gauche (gg) and (d) "kink" (gtg').
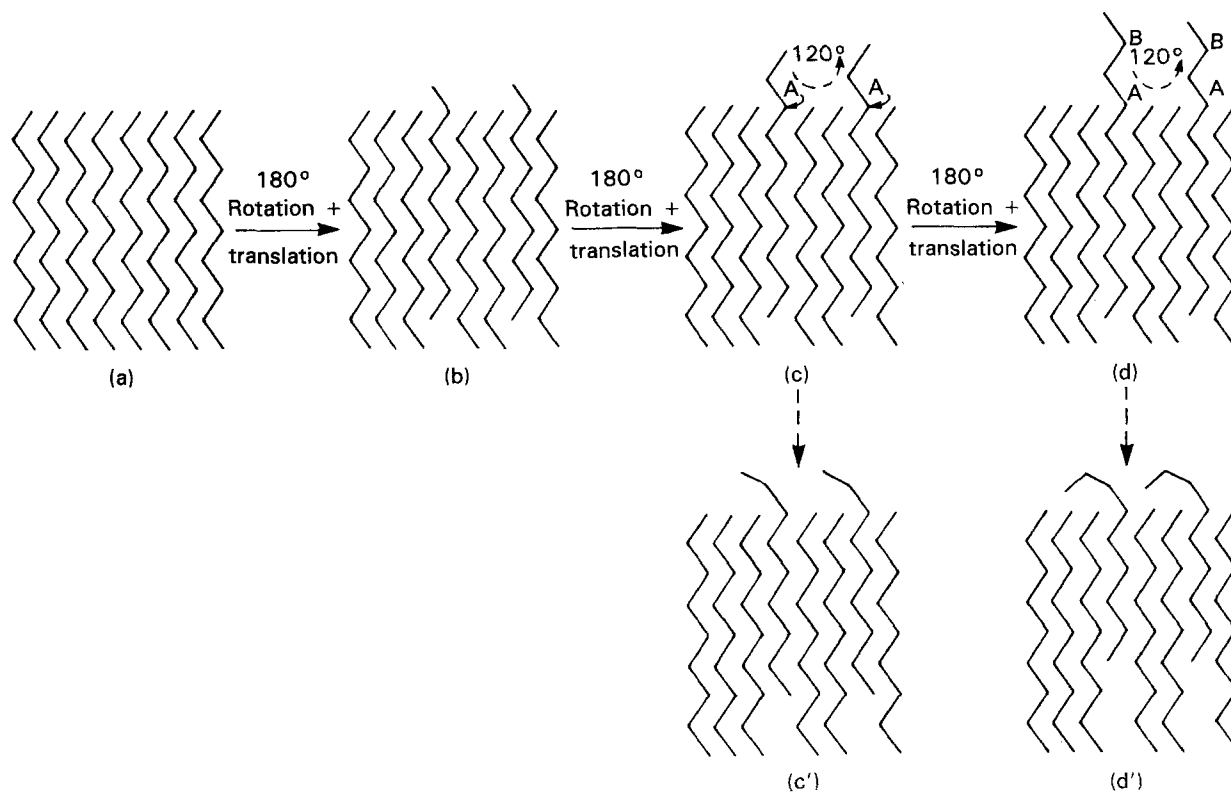
Fig. 3. In this we see that void formation within the solid structure would accompany the rotation–translation process with such gaps enabling an inter-chain mixing process as the displaced groups from adjacent crystallites fill the voids. In the case of homologous mixtures, the displaced groups are likely to be present from the onset, and so the conformational disorders will already exist. This chain rotation mechanism is, therefore, not required for the folding process in such mixtures. In this paper we seek to define such molecular conformational disordering by using Fourier transform–infrared (FT–IR) spectroscopy to examine a range of n-alkanes and mixtures of homologues in order to define the influence of factors such as chain length and chain-length distribution on this disordering process.

2. Experimental procedure
2.1. Sample preparation
A number of crystalline materials were prepared and analysed:

(a) single n-alkanes; $C_{20}H_{42}$, $C_{21}H_{44}$, $C_{36}H_{74}$ and $C_{50}H_{102}$;

(b) binary mixtures; $C_{20}:C_{22}$ in the ratio 67:33 and 40:60;

(c) a tertiary mixture; $C_{19}:C_{20}:C_{21}$ in the ratio 19:21:60;

(d) multihomologous mixtures (waxes) with mean carbon chain lengths of; 18.3, 21.3, 21.5, 21.6, 22.0, 22.7, 22.8, 23.2, 24.7, and 26.9.

n-Alkanes, binary and tertiary mixtures; gas chromatographs showed all samples to be greater than 99% pure [27].

Figure 2 Schematic representation of chains consecutively undergoing the rotation–translation process. Steps (a–d); chain undergoes a rotation of 180° with respect to the carbon axis accompanied by a translation along the chain by one carbon atom. Steps (c–c') and (d–d'), bonds A and B in the displaced section of chain, now free from the constraints of the crystal lattice, undergo a rotation of 120° with respect to the carbon chain, thus introducing gauche defects into the systems; resulting in (c') end-chain twisting and (d') end-chain folding.
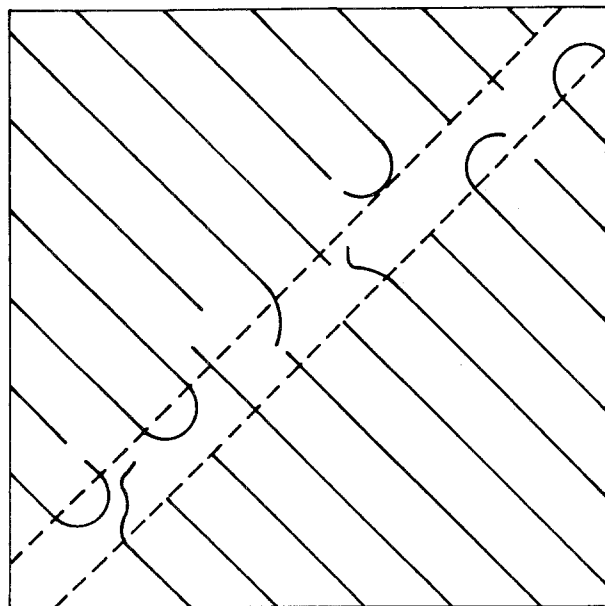
Figure 3 Illustrative model of the effect of chain folding and end-chain bending, as found in polyethylene crystals, on the packing of the interlamellar region; (a) straight lines represent all-*trans* chains which pack adjacently in the crystal. An ill-defined interlamellar region is formed as a result of the poor packing introduced by the defects described above.

The multihomologous waxes were supplied by Exxon Chemical Ltd.

2.2. FT–IR spectroscopic measurements

FT–IR spectroscopic measurements were carried out using a Nicolet 20 SXB FT–IR Spectrometer over the spectral range $1400-700\ cm^{-1}$; a region considered the fingerprint region being associated with C–H wagging, rocking and stretching vibrational modes [18–20]:

1. *trans*-gauche (tg) $(\sim 1345, 1167, 1079, 960, 908$ and $878\ cm^{-1})$
2. double gauche (gg) $(\sim 1354$ and $898\ cm^{-1})$
3. "kink" (gtg') $(\sim 1367$ and $1308\ cm^{-1})$

Most of the conformationally sensitive bands arising in this region are weak; as a result substantial samples, which consisted of approximately 500 µm thick films sandwiched between sodium chloride windows, were required. These films were prepared by pipetting the molten alkane(s) on to the sample plate which was then secured by a second plate separated by a 500 µm thick teflon spacer; the film was then left to equilibrate at room temperature for 3 days.

All FT–IR data were obtained at room temperature with the samples in the low-temperature phase (phase I).

3. Results and discussion

The data are summarized in Table I and Fig. 4.

3.1. Normal alkanes

As would have been expected from previous work [14–23], FT–IR data for C_{20} and C_{21} provided no indication of non-planar (gauche) conformers. A weak band did appear at $1345\ cm^{-1}$ for n-C_{21} which would imply the presence of a tg conformer. In this case, however, this band corresponds to a methylene wagging mode of vibration [20].

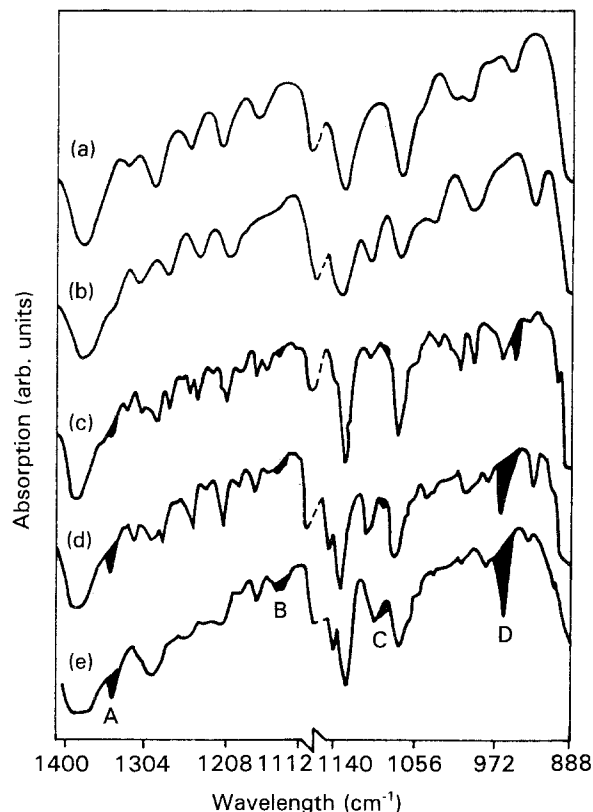$C_{36}H_{74}$ has a very low concentration of tg conform-

Figure 4 Comparison of the FT–IR spectra of (a) $C_{20}H_{42}$, (b) $C_{21}H_{44}$, (c) C_{20}:C_{22} (67:33), (d) C_{19}:C_{20}:C_{21} (19:21:60), and (e) wax (mean carbon chain length = 18.3). Strongest bands resulting from tg conformers are shaded: (A) 1345. (B) 1167, (C) 1079 and (D) 960 cm^{-1}.

ers, shown by the appearance of weak bands at 1144 and $962\ cm^{-1}$. $C_{50}H_{102}$, on the other hand, has a much higher concentration of tg conformers illustrated by the increased intensity of the previous peaks and, in addition, the appearance of several more $(1167, 1077, 908$ and $878\ cm^{-1})$. Additional bands associated with gg and gtg' conformers also appeared (at 1345, and 1367 and $1308\ cm^{-1}$, respectively).

The presence of a small concentration of double gauche bonds in crystals of n-C_{50} would suggest that some chain folding had been incorporated into this system. Such a process has been identified in long alkanes of greater than one hundred carbon atoms chain length, as described earlier, but has not been shown to exist in short alkanes at such low temperatures.

End-chain twisting (as observed in n-C_{36} and n-C_{50}) could be considered the first step towards a partial chain-folding process. For such a process to occur, the chain ends in these crystals must become more mobile (i.e. less restricted by the strong intermolecular forces binding adjacent molecules in the crystal lattice). This increased mobility may have been achieved in two ways; surface melting at the lamellar interface and/or displaced groups resulting from the rotation–translation process.

The long n-alkanes which exhibit the phenomena of chain folding are also capable of a process referred to as "isothermal thickening" at the crystallization temperature [28]. This involves the transition between the once folded system to the thermodynamically more stable fully extended chain crystals (i.e. the process is reversible).

TABLE I Observed frequencies of vibrational bands resulting from the three non-planar conformers; trans-gauche (tg), double gauche (gg) and "kink" (gtg'): (vw = very weak, w = weak, m = medium, s = strong and vs = very strong – in reference to intensity of absorption band). Calculated frequency/cm^{-1}

			1345	1167	1079	960	908	878	1354	898	1367	1308
			(tg)						(gg)		(gtg')	
SAMPLES												
(A)	(B)	(C)										
20	0	1	—	—	—	—	—	—	—	—	—	—
21	0	1	1344w	—	—	—	—	—	—	—	—	—
36	0	1	1344w	—	—	962w	—	—	—	—	—	—
50	0	1	1344w	1167w	1077m	962w 957m	908vw	878vw	1354w	—	1367vw	1308w
20.6	0.92	2	1344m	1164m 1169vw	1079vw	962s 957w	904m	878vw	1353w	—	1365vw	1308m
21.1	0.97	2	1344m	1164vw 1169w	1079w	962s 957m	908vw 904m	876vw	1353w	—	1365w	—
20.2	0.66	3	1344s	1164m	1077m 1079vw	957vs	908w 904w	876w	1354w	—	1365w	1308vw
18.3	3.96	13	1344vs	1167w 1169m	1079w	957vs	905m	876vw	1353w	900vw	1365w	1308w
21.3	5.48	17	1344s	1169s 1164w	1079w	957vs	904w	876vw	1354w	—	1365w	1308w
21.5	2.91	13	1344s	1169s 1164m	1079w	962vw 957vs	908w 904w	878w	1353m	869vw	1365m	1308w
21.6	3.68	13	1344s	1169s 1164w	1079vw	957vs	908w 904w	—	1353m	—	1367m	1310w
22.0	3.47	11	1344s	1169s 1164m	1079vw	957vs	906vw	878vw	1353vw	—	1365m	1308w
22.7	4.57	16	1344s	1169s 1164w	1079vw	962vw 957vs	904w	876w	1353vw	—	1365w	1308vw
22.8	4.98	13	1344s	1169s 1164m	1079w	957vs	904w	876vw	1353vw	—	1365w	1309w
23.2	6.07	19	1344m	1169s	1077s	957vs	904w	—	1354vw	—	1365vw	—
24.7	7.71	15	1344m	1169s 1164m	1079s	957vs	904w	—	1353vw	—	1365w	—
26.9	11.41	18	1344m	1169s	1079s	957vs	904vw	—	1353vw	—	1365w	—

[(A) Mean carbon chain length, (B) Variance, (C) Number of homologues]

There must exist a transition stage between chains that can undergo the folding process and those which form very stable all *trans* structures and as a result do not chain fold. This partial melting at the chain ends, shown here to exist in small concentrations in crystals of *n*-alkanes as short as *n*-C$_{36}$, may describe the process exhibited within this transition period. This surface-melting phase may simply result from the formation of a surface rotator phase. The hindered rotation of the chain ends, in some cases, may possess enough energy to drag round the remainder of the chain, thus incorporating the rotation–translation process. A combination of these effects will likely be in play.

3.2. Binary and tertiary homologous mixtures
The binary and tertiary mixtures had all the bands associated with the disorder found in *n*-C$_{50}$ but with an increased intensity. The partial melting process we suggest will occur in the solid-state structures of alkanes $\geqslant$ C$_{36}$; these systems consisted of short chain alkanes ($\leqslant$ C$_{22}$) thus surface melting is unlikely to be a contributing factor.

Consider the effect of chain-length inhomogenieties on the concentration of non-planar conformers present in the crystal systems analysed. As the number of homologues of different chain lengths in a mixture increase, the concentration of tg and gg conformers increase. This can be explained quite simply in terms of near-neighbour interactions.

Consider the simplest case: a 1:1 mixture of two *n*-alkanes of different chain lengths (differing by only two carbon atoms) co-crystallized together. In the crystalline solid solution formed the two alkanes will, on average, occupy adjacent sites within the crystal lattice with the chain directions perpendicular to the lamellar surface, both adopting the overall *trans* conformation. Because the chains differ by two carbon atoms, at alternating sites on the lamellar surface an ethyl group will be exposed. These chain ends will be free from the constraints of the crystal lattice and will be able to move more easily. The displaced groups, in order to achieve a thermodynamically more favourable state, will try to enter the crystal lattice; this can be achieved in two ways: the groups could merge with an adjacent lamella or "twist back" from the inter-lamellar region into the close packed structure (thus resulting in a tg conformer, cf. Fig. 3).

As the number of components in a mixture increases, the number of methylene groups displaced at the surface will vary and the types of conformers attainable at the chain ends will increase.

3.3. Multi-homologous mixtures
Bands associated with tg and gtg' conformers were observed for all the multi-homologous waxes with

approximately constant intensity, decreasing slightly as the chain length increased. The relative intensity of the bands associated with the gg conformer, however, although always present, were reduced as the mean carbon chain length increased. This result does not mean that the concentration of these conformers present decreases with increasing average chain length. The intensity of the non-planar bands are relative to the background absorption, i.e. absorption due to the all-*trans* structure. As the number of carbons in the chain increases, the amount of absorption due to the overall *trans* structure will increase. Thus the intensity of the non-planar bands relative to the background will decrease. Therefore, a quantitative comparison of the defects introduced in relation to the mean carbon chain length cannot be achieved in this way.

If waxes (mean carbon number) 21.3, 21.5 and 21.6 are only considered, then the influence of variance of the chain length distribution could be obtained because over such a narrow range the effect of peak quenching from the background can be ignored. The variance, σ^2, is defined as

$$\sigma^2 = \sum_{i=1}^{n} (x_i - \mu)^2 f(x_i) \qquad (1)$$

where μ is the mean carbon chain length, x_i is the carbon number and $f(x_i)$ is the normalized weight per cent of carbon number, i.

For wax 21.5 (variance 2.91), several bands appear stronger (1164, 962, 878 and 869 cm^{-1}, see Table I) than for waxes 21.3 and 21.6 which have higher variances (5.48 and 3.68 respectively). Therefore, wax 21.5 apparently has a much higher concentration of end-chain defects than the other two waxes.

Interchain mixing would reduce the amount of end-chain disorders as the displaced groups find an alternative route, other than chain twisting, to enter the stable crystalline structure. It can be suggested from this that perhaps the broad distribution waxes accommodate more easily the interchain mixing process than the narrower distribution waxes.

4. Conclusion

The FT–IR analysis of the alkanes considered here has shown that end-chain defects have been incorporated into the solid-state structures of single alkanes $\geqslant n$-$C_{36}H_{68}$; as the alkane chain length increases the number of defects increases and as the number of different homologues in the crystals increase the concentration of non-planar conformers present increases.

For the single alkanes, partial melting of the chain ends at the lamellar surface would likely account for the presence of such defects (preferential melting of the surface; bulk remains in the stable crystalline state). It is possible, however, that chain twisting resulting from displaced groups at the lamellar surface following a rotation–translation process will also contribute to the disorder.

For the mixtures, chain-length mismatches resulting in displaced ethylene groups at the crystal surface which undergo processes such as twisting, folding and interchain mixing as they try and enter the stable crystalline environment, would account for the disorders observed here.

A combination of effects (surface melting, rotation–translation processes and chain-length inhomogeneities), result in end-chain folding/twisting in crystals of alkanes thus leading to a disruption of the inter-lamellar packing, effectively creating an amorphous film between crystals.

References
1. D. M. SMALL, "The Physical Chemistry of Lipids" (Plenum Press, New York, 1986).
2. G. R. STROBL, *J. Polym. Sci. Polym. Symp.* **59** (1977) 121.
3. R. D. HEYDING, K. E. RUSSELL, T. L. VARTY and D. St-CYR, *Powder Diffrac.* **5**(2) (1990) 93.
4. M. G. BROADHURST, *J. Res. Nat. Bur. Stand.* **66A** (1962) 241.
5. H. E. KING, E. B. SIROTA, H. SHAO and D. M. SINGER, *J. Phys. D: Appl. Phys.* **26** (1993) B133–B136.
6. P. C. PAINTER, J. HAVENS, W. W. HART and J. L. KOENIG, *J. Polym. Sci.* **15** (1977) 1223.
7. S. J. SPEELS, S. J. ORGAN, A. KELLER and G. ZERBI, *Polymer* **28** (1987) 697.
8. G. UNGAR and S. R. ORGAN, *Polym. Commun.* **28** (1987) 232.
9. G. ZERBI, *J. Appl. Chem.* **26** (1971) 499.
10. R. G. CHAMBERS, J. E. ENDERBY, A. KELLER, A. R. LANG and J. W. STEEDS (eds), "Sir Charles Frank, OBE, FRS: An eightieth birthday tribute" (Bristol, Philadelphia, New York, 1991).
11. G. UNGAR and A. KELLER, *Polymer* **27** (1986) 1835.
12. G. UNGAR, J. STEJNY, A. KELLER, I. BIDD and M. C. WHITING, *Science* **229** (1985) 386.
13. C. S. YOON, J. N. SHERWOOD and R. A. PETHRICK, *J. Chem. Soc. Farad. Trans. I.* **85** (1989) 3221.
14. H. L. CASAL, D. G. CAMERON and E. C. KELUSKY, *J. Chem. Phys.* **80** (1984) 1407.
15. E. C. KELUSKY, I. C. P. SMITH, C. A. ELLIGER and D. G. CAMERON, *J. Am. Chem. Soc.* **106** (1984) 2267.
16. H. G. OLF and A. PETERLIN, *J. Polym. Sci. A-2* **8** (1970) 791.
17. M. G. TAYLOR, E. C. KELUSKY, I. C. P. SMITH, H. L. CASAL and D. G. CAMERON, *J. Chem. Phys.* **78** (1983) 5108.
18. M. MARONCELLI, S. P. QI, H. STRAUSS and R. G. SNYDER, *J. Am. Chem. Soc.* **104** (1982) 6237.
19. R. G. SNYDER, *J. Mol. Spec.* **4** (1960) 411.
20. Idem, *J. Chem. Phys.* **47** (1967) 1316.
21. R. G. SNYDER, M. MARONCELLI, S. P. QI and H. L. STRAUSS, *Science* **214** (1981) 188.
22. R. G. SNYDER, M. MARONCELLI, H. STRAUSS, C. A. ELLIGER, D. G. CAMERON, H. L. CASAL and H. H. MANTSCH, *J. Am. Chem. Soc.* **105** (1983) 134.
23. G. ZERBI, R. MAGNI, M. GUSSONI, K. MORITZ, A. BIGOTTO and S. DIRLIKOV, *J. Chem. Phys.* **75** (1981) 3175.
24. M. MARONCELLI, H. STRAUSS and R. SNYDER, *J. Phys. Chem.* **89** (1985) 4390.
25. Idem. ibid. **89** (1985) 5260.
26. S. BLASENBREY and W. PECHHOLD, *Rheol. Acta.* **6** (1967) 174.
27. A. GERSON, PhD thesis, University of Strathclyde (1991).
28. S. J. ORORGAN, G. UNGAR and A. KELLER, *J. Polym. Sci.* **B-28** (1990) 2365.