Geometrical limits to order in liquid crystalline random copolymers

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The paper investigates the limits of solid state order which are physically possible on cooling thermotropic random copolymers from the liquid crystalline phase. The work extends earlier studies which have explored the limiting situation in conventional non-mesogenic random copolymers where only one component is considered crystallizable. The rigid nature of the polymer chains considered in this exercise has encouraged the development of a two dimensional computer modelling routine (Domino). Order associated with matches between adjacent molecules in a model is determined for both the quenched condition (Wunderlich's cold crystallization[7]) and the searched condition which produces better matches by permitting particular levels of chain mobility and is closer to Flory's equilibrium theory of crystallization[4]. The approach used involves finding the largest matching sequence between adjacent chains for a given set of conditions, and then noting all possible secondary matches. The matches found may be between regular sequences (i.e. -AAAAAA-, -BBBBBB- or -ABABAB-) or random sequences (e.g. -ABBABAAB-). Where matches between successive pairs of chains are opposite each other, they propagate laterally to give two dimensional 'crystalline' regions. Propagation of a particular random sequence gives rise to non-periodic layer (NPL) crystals, which have been discussed previously[18]. Models have also been examined with chains built on the basis of non-random statistics. The variation in the extent of ordered regions has been explored as a function of the chain composition, chain randomness, relative motion between chains, relative lengths of units and axial variability of unit lengths. For the case of random chains without searching, the model parameters have been compared with those predicted on the basis of statistical analysis. The agreement is good. A probabilistic approach to 'searching' has revealed considerable dependence on the particular search routine used, and the fact that the easiest situation to calculate will not necessarily be the most realistic. The results are discussed briefly in the context of experimental data from a thermotropic random copolyester of hydroxybenzoic and hydroxynaphthoic acids.

(Keywords: random copolymer; liquid crystalline polymer; thermotropic mesophase; computer modelling; chain statistics; NPL crystallites)

INTRODUCTION

The issue is order in random copolymers. Chains in which two or more different types of chemical unit are joined in a random sequence are not able to contribute fully to the three-dimensional periodicity of a crystal lattice. However, isolated regions of order can be envisaged under some circumstances, and this paper describes a simple model designed to explore both the type and extent of the order which may be present. The fact that attention has been focused on the problem by the observed behaviour of rigid-chain random copolymers which melt to give a liquid crystalline phase, does not limit the relevance of the model to this class of polymer. Flexible chain random copolymers and atactic homopolymers may also be subject to the same principles, although chains which align parallel in the melt form the most comfortable basis for the model.

The central questions asked are first, given that a random copolymer chain will have, by chance, a certain proportion of runs of like units which exceed a given length, to what extent is it possible for such runs to segregate and form perfect, albeit small and isolated, crystallites? Second, is it possible for identical but random sequences to segregate and thus propagate lateral order in a unit which is aperiodic in the direction of the chain axis? Such a sequence matching process might be seen to have more in common with biological molecules than synthetic polymers.

The limits to which such processes are possible, in purely geometric terms, are explored by building computer models of systems of chains, and in some cases comparing the results with statistical calculation. Experimental indications of order in rigid chain random copolymers are summarized, and the relevance of the model predictions to these observations is discussed.

BACKGROUND

The question of crystallization of one component of a random copolymer was first addressed by Flory[1], and the study was extended in subsequent publications[2–5]. The thermodynamic treatment was based on the premise that homopolymer sequences in random copolymer chains are able to segregate and crystallize. The model thus takes no account of any kinetic or geometric constraints, due to the fact that the sequences are part of a chain, on the formation of the crystallites. The approach led to the prediction of a decrease in melting point with increasing

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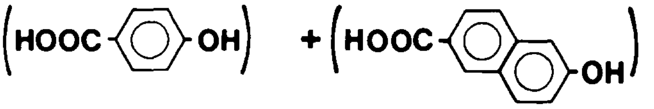

Figure 1 Monomer units of hydroxybenzoic acid and hydroxynaphthoic acid

concentration of the second 'non-crystallizable' component in the random chain, as expressed by the well known equation:

$$\frac{1}{T_\mathrm{m}}-\frac{1}{T_\mathrm{m}^0}=-\frac{R}{\Delta H_\mathrm{u}}\cdot\ln(P) \qquad (1)$$

where T_m^0 is the melting point of the pure homopolymer, and T_m that of the copolymer. ΔH_u is the enthalpy of fusion per mole of crystallizable units, and R is the gas constant. P is the probability that one crystallizable unit follows another, and for random chains will be equal to the mole fraction of such units.

The predicted, depressed, melting point T_m corresponds to the melting of the largest crystallites incorporating the longest sequences in the chains, but as their volume fraction is low it is made clear[3] that it will be difficult to detect this limiting temperature experimentally. Indeed, it is referred to as the temperature of incipient crystallization[4]. Measured melting points[5] are lower than those predicted, not only for this reason, but also because of the presence of both kinetic and geometrical constraints in real systems. Interestingly, other authors[6] have used equation (1) to demonstrate that supposedly atactic PVC chains actually contain substantial sequences of syndiotactic units.

In the absence of constraint, these approaches predict that, at sufficiently low temperature, all of the crystallizable component of the random chains will in fact have crystallized. The predicted crystallinity thus is equivalent to the concentration of the component. This assumption has been highlighted by Wunderlich[7], who considered the case of total constraint, in which no segregation of sequences of like units is deemed possible. The crystallinity is very much lower than in the equilibrium case, especially when the number fraction of crystallizable units drops below 0.7. This totally constrained process was called 'cold crystallization'. Attempts to explore the influence of constraints have led to consideration of the incorporation of units of one type into crystals of the other as defects [8-12]. A capacity for defects within the crystals will reduce the limiting influence of kinetic and geometric constraints on the crystallinity observed under any particular set of conditions.

The model developed below is specific in that it enables the prediction of homopolymer crystallinity for defined conditions of the geometrical constraint by virtue of the incorporation of the units into the chains, and of the kinetic constraint whereby conditions can be explored ranging from '*quenched*' which bears a close relationship to Wunderlich's 'cold crystallization'[7], to partially '*segregated*' according to predefined rules. At this stage the model is used only to predict limits of crystalline type order and has not yet been developed as the basis for predictions of melting points. However, it has proved possible to study the influence of non-random arrangements of units, 'blockiness', on the level of order obtainable, and to review carefully the geometric factors governing the lateral register of given random sequences along the chain, to form what are known as non-periodic layer (NPL) crystallites.

A MODEL TO SIMULATE CHAIN ORDERING IN COPOLYMERS—(DOMINO*)

Chain parameters

The chains used in the model are straight random sequences of two different units of different length, there is otherwise no chemical detail. The chains are thus represented as sequences of A and B. Such chains are a simple analogue of comparatively straight random copolymer chains employed in many types of liquid crystalline thermoplastic. A particular example of such a polymer is the copolyester of hydroxybenzoic and hydroxynaphthoic units which have approximate lengths of 0.63 and 0.83 nm (*Figure 1*).

The parameters used in this study, which are varied at appropriate stages, are:

1 Lengths of A and B units.

2 Relative proportions of A and B. This is called the chain composition and is defined as the number fraction of A units, X_A and of B units, X_B.

3 Departures from random statistics whereby the probability of a unit occurring at a particular position depends not only on the overall composition but on the nature of the previous unit in the chain. Where the probability of like following like is enhanced, the chain is said to become 'blocky'. Where dissimilar pairs are more probable than similar, the chain is described as 'antiblocky'. In the limit, 'blockiness' would imply a block copolymer with long runs of each type of homopolymer, whereas 'antiblockiness' would tend to a regular 'AB' or alternating copolymer, at least for $X_\mathrm{A}=X_\mathrm{B}=0.5$.

Chain building

For any copolymer chain, the ratio of probabilities:

$$R_\mathrm{P}=\frac{P_{AA}+P_{BB}}{P_{AB}+P_{BA}} \qquad (2)$$

where P_{ij} is the probability of unit i following unit j along the chain, may be used to describe the degree of 'blockiness'. In the special case of $X_\mathrm{A}=0.5$, R_P will be unity for a random chain. It will tend to infinity for a very blocky chain, and zero for an alternating copolymer. A blocky chain may thus be built by biasing the random number generator in favour of A following A and B following B.

In order to be able to predict the value of P_{ij} and hence R_P for any given amount of bias, it is helpful to consider the copolymerization reaction kinetics developed by Dostal[13], Alfrey and Goldfinger[14], Mayo and Lewis[15], Simha and Branson[16] and Wall[17], which yielded the 'copolymer equation':

$$\frac{\mathrm{d[A]}}{\mathrm{d[B]}}=\frac{[\mathrm{A}]}{[\mathrm{B}]}\cdot\frac{r_\mathrm{A}[\mathrm{A}]+[\mathrm{B}]}{[\mathrm{A}]+r_\mathrm{B}[\mathrm{B}]} \qquad (3)$$

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* The name Domino stems from analogy with the game 'Dominoes'. The program runs on an Acorn Master microcomputer

where $r_i = k_{ii}/k_{ij}$, k_{ij} being the rate constant for a reaction in which a monomer j reacts with a chain terminal group i. The square brackets denote concentrations and for simplicity we consider only the case when $r_A = r_B$ ($=r$). If [A] and [B] are considered to be 'feed' concentrations for the building process (in mole fractions), then the ratio of A to B in the chain formed at any instant is given by d[A]/d[B]. Since we may assume infinite reservoirs of monomers A and B, [A] and [B] may be considered constant, as may d[A]/d[B], which may be replaced by X_A/X_B. Equation (3) becomes:

$$\frac{X_A}{X_B} = \frac{[A]}{[B]} \cdot \frac{r[\mathrm{A}]+[\mathrm{B}]}{[\mathrm{A}]+r[\mathrm{B}]} \tag{4}$$

and relates the feed composition to final chain composition via the ratio of rate constants, r. The rate of production of j-units following i-units on a chain is given by:

$$\Theta_{ij} = k_{ij}[j][\text{chains terminating in } i] \tag{5}$$

The probability of finding a j-unit following an i-unit in a chain will be given by the relative rate of formation (normalized so that $\sum_{i,j} P_{ij} = 1$), i.e.

$$P_{ij} = \frac{\Theta_{ij}}{\sum_{k,l} \Theta_{kl}} \tag{6}$$

Thus equation (2) becomes:

$$R_P = \frac{\Theta_{AA} + \Theta_{BB}}{\Theta_{AB} + \Theta_{BA}} \tag{7}$$

The steady-state condition is that the concentration of chains terminating in a particular unit should remain constant. Therefore, the rate of change of end group type from A to B must equal the rate of change from B to A. Hence $\Theta_{AB} = \Theta_{BA}$, and substituting for Θ_{ij} from equation (5) gives:

$$R_P = \frac{r}{2} \cdot \frac{[\mathrm{A}]^2 + [\mathrm{B}]^2}{[\mathrm{A}][\mathrm{B}]} \tag{8}$$

So, if we specify the required blockiness R_P and chain composition X_A, we are able to calculate, using equations (4) and (8), the feed composition [A] and the rate factor r, subject only to the constraint:

$$R_P \geqslant \frac{2X_A - 1}{2(1 - X_A)} \quad ; \quad [X_A \geqslant 0.5] \tag{9}$$

which follows from substituting equation (4) into equation (8).

In order to use this information to build a chain, we consider that we have a chain terminating in a particular unit i, and we evaluate the probability of the next unit being a j:

$$\Psi_{ij} = \frac{\Theta_{ij}}{\sum_k \Theta_{ik}} \tag{10}$$

Hence,

$$\Psi_{ij} = \frac{r[i]}{r[i] + [j]} \tag{11}$$

i.e.

$$\Psi_{AA} = \frac{r[\mathrm{A}]}{r[\mathrm{A}] + [\mathrm{B}]} \quad ; \quad \Psi_{AB} = \frac{[\mathrm{B}]}{r[\mathrm{A}] + [\mathrm{B}]}$$

$$\Psi_{BA} = \frac{[\mathrm{A}]}{[\mathrm{A}] + r[\mathrm{B}]} \quad ; \quad \Psi_{BB} = \frac{r[\mathrm{B}]}{[\mathrm{A}] + r[\mathrm{B}]} \tag{12}$$

From the above analysis we conclude that ideal chains ($r = 1$) of composition $X_A = 0.75$ and 0.9, have $R_P = 1.67$ and 4.56, respectively. So we define a new parameter R'_P:

$$R'_P = R_P / R_P^{\text{ideal}} \tag{13}$$

which gives the blockiness of a non-random chain relative to an ideal random one of the same composition.

The random number generator used to produce the random copolymer chains was tested over many tens of thousands of numbers in a check to see if there was any systematic bias in the blockiness of the chains produced. Any variations found were shown, using the χ^2 test, to be not significantly different from the ideal case. We therefore conclude that the results described here are not coloured in any way by any difficulty in building genuinely random chains.

Chain matching

Consider the random sequences of A and B units placed side by side in *Figure 2a*. The longest match of a homopolymer sequence is marked (i), and the longest match of any sequence is marked (ii). In either case the match is referred to as the primary match. The primary match does not depend on the relative lengths of A and B units; it is sufficient that they are distinguishable. Also noted on *Figure 2a* are potential secondary matches, based on any matching sequence of two or more units. These are potential matches only for the primary match is seen as locking the exact relative positions of the chains, and hence a secondary match is only achieved when the total lengths of the units separating it from the primary match are either equal for each chain, or differ by an integral number of unit lengths. The matching program seeks secondary matches by moving along the chains away from the primary match and noting where there are identical sequences in register to within a predefined distance.

In any real system molecular mobility will provide the opportunity for chains to 'search out' better matches. Conceivably, this can occur by chains moving lengthwise with respect to each other as well as interchanging neighbours. The 'Domino' search routine steps one chain past the other (taking units off the bottom and putting them on the top) and records the best primary match found. The number of unit steps taken is known as the search length, and can be set at any value up to the length of the chain, which was fixed at 100 units for all the modelling calculations. *Figure 2b* shows the best primary match for any sequence after a 100 unit search, and also potential secondary matches. Not surprisingly, the

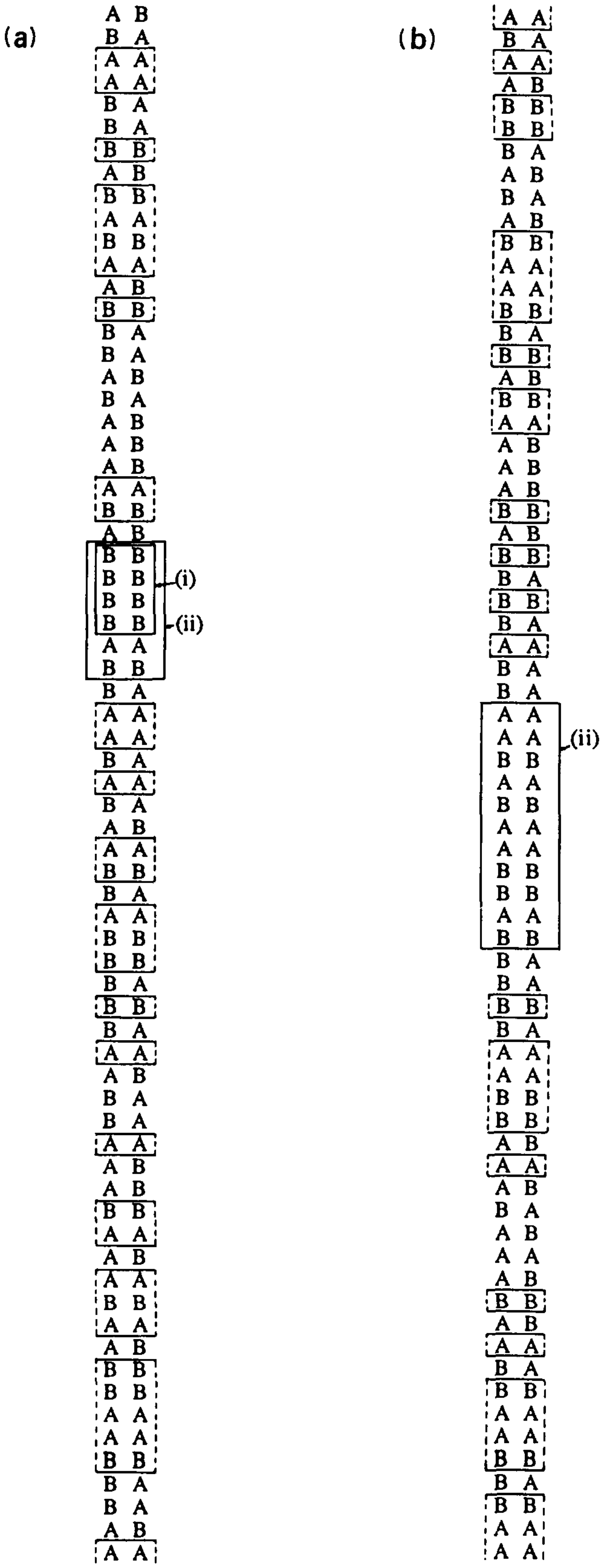

Figure 2 (a) Part of a pair of random chains, with units denoted by A and B, showing (i) the best homopolymer match and (ii) the best match of any kind. Potential secondary matches are also shown as broken boxes. (b) The same chains after searching. The best match is marked (ii)

primary match is longer than in *Figure 2a*. The best primary match of homopolymer sequences is not shown in *Figure 2b* as it occurred with the chains in a different relative position to that depicted. When the search length is zero, the chain model will be referred to as 'quenched', whereas after a 100 unit longitudinal chain search it will be described as 'searched'.

The longitudinal movement of chains relative to each other is but one realistic searching process. During the slow crystallization of a rigid chain random copolymer, there is also the possibility of lateral sorting whereby neighbouring molecules diffuse past each other until a match of suitable quality is found. Lateral sorting is not statistically equivalent to longitudinal searching, although the end result will be qualitatively similar in that the length of primary matches will be improved. The difference between the two possible searching routines is discussed later, in the context of algebraic solutions.

The number and size of secondary matches should not, on average, be affected by trying different relative positions of the chains in a search procedure, except that where searching leads to a longer primary match, there will be somewhat less chain length available for secondary matches. Of the three chain parameters listed above, the relative lengths of the units will only influence secondary matches, while chain composition and blockiness will affect both primary and secondary matches.

It should be noted that the approach which looks for the longest perfectly matched sequences is only one of several strategies. One could obviously set other criteria such as maximizing the number of like unit contacts between two chains within a particular error allowance. The philosophy adopted here is to find the limiting extent to which crystalline order is possible. If one permits defects within the crystals then, because of the statistical framework of the problem, the degree of 'crystallinity' obtained could appear significantly larger.

RESULTS OF COMPUTER MODELLING

All the results in this section are based upon two-dimensional models with 100 chains each of 100 units and except where stated, units of length 0.63 and 0.83 nm. The most important parameter required to describe primary matches is the mean match length, in numbers of units, expressed as a percentage of the length of each chain. This is called the primary match density, $L(\%)$. The 100 chain model appears sufficiently large to give representative values of the match density. Building successive models with the same chain parameters leads to match densities which vary by not more than a few per cent, although the variation is observed to increase on moving to extremes of composition or blockiness. Each numerical result shown in the figures was obtained by averaging three chain models. It should be emphasized that the primary match density will not be proportional to the chain length, and this aspect is explored through an algebraic approach described later.

Regular primary matches

Three types of regular primary matches are considered: those consisting of [–AAAAAA–] homopolymer sequences, those of [–BBBBBB–] sequences, and those comprising an alternating [–ABABAB–] sequence. The latter are of special significance when anti-blocky chains

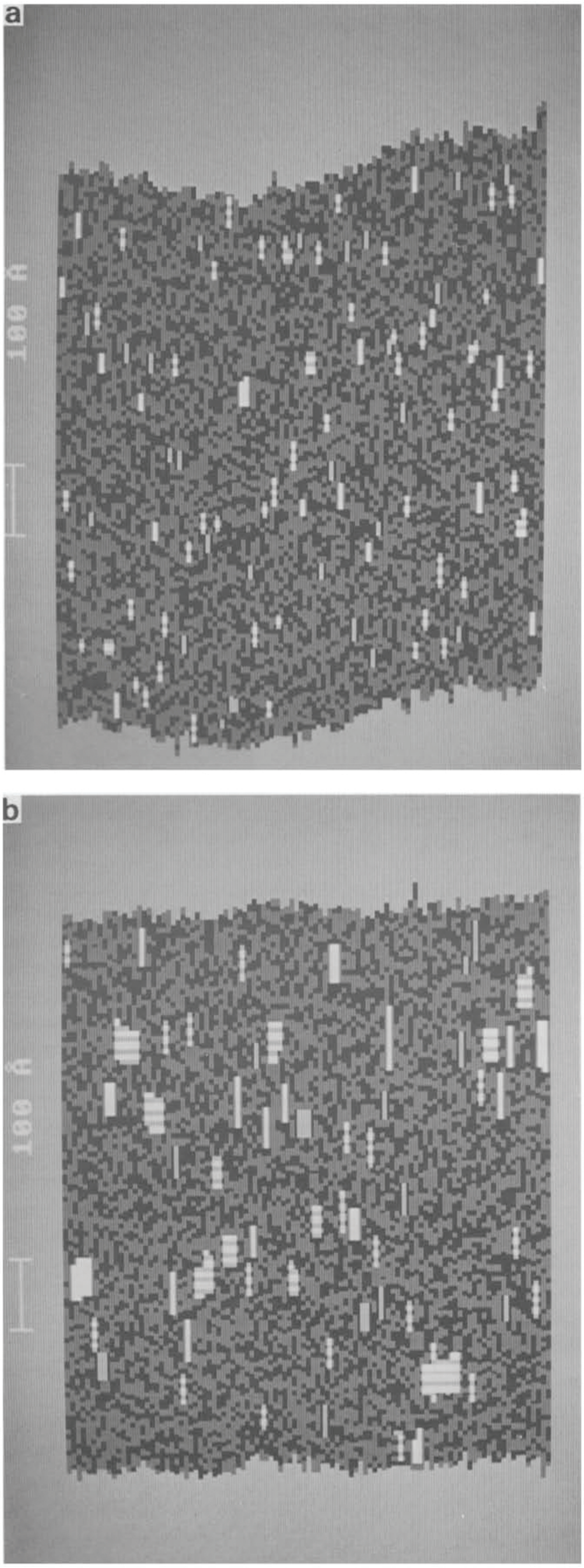

Figure 3 Plots of 100 random 100 unit copolymer chains, with $X_A=0.5$, showing homopolymer and AB regular primary matches: (a) no search, and (b) a search of 100 units. Unit A is shown in black, whereas unit B is dark grey. The matches are highlighted by altering the colours of the matching units from black to light grey, and from dark grey to white. The very thin vertical lines are the screen raster and should be ignored

are considered. In this context, the search for a regular match could mean any of the above sequence types being found, whichever is the longer. Thus, $L(\%)$ may be broken down into three components, such that $L(\%)=L_A(\%)+L_B(\%)+L_{AB}(\%)$, where $L_A(\%)$, $L_B(\%)$ and $L_{AB}(\%)$ are match densities for homopolymer A, homopolymer B and AB regular sequences, respectively.

Random chains without searching. A quenched model with 100 chains each of 100 units is shown in *Figure 3a*. It was built by adding successive chains from left to right. The chains are random with equal proportions of A and B units ($X_A=X_B=0.5$). There has been no searching to optimize the match. Where there is a primary match this is emphasized in the figure by altering the tonal density of the matching units: black units become light grey, and dark grey units become white. The match densities are $L_A(\%)=0.95\%$, $L_B(\%)=1.07\%$ and $L_{AB}(\%)=1.97\%$.

Figure 4a shows the effect of variation in chain composition X_A on $L_A(\%)$, $L_B(\%)$, $L_{AB}(\%)$ and $L(\%)$. Not surprisingly the match densities increase towards 100% as the chain compositions approach 100% A or 100% B. It is interesting to note that the primary matches rapidly become either completely type A or completely type B as the chain composition changes from exactly 0.5.

The effect of searching. Figure 3b shows the model with parameters as for *Figure 3a* ($X_A=X_B=0.5$, random chains) except that the primary matches are the best found in each 100 unit search. They are longer: $L_A(\%)=1.26\%$, $L_B=1.66\%$ and $L_{AB}(\%)=3.42\%$. *Figure 4b* shows again the influence of chain composition. The effect of different search lengths up to 100 units, on the match densities for three chain compositions, $X_A=0.5$, 0.75 and 0.9, is illustrated in *Figure 5*.

Nucleation weighting. Although one can view the chains modelled in *Figure 3* as being tacked together by matching sequences, the order is not sufficiently extensive to be thought of as microcrystallinity. However, it is a basic premise that ordered regions, once established, will grow in preference to the formation of new entities. In other words there is a barrier to nucleation. Without assessing the size of any such barrier in the case of rigid chain polymers, the effect of various levels of nucleation weighting on the appearance of the matched regions was explored through the simple expedient of 'scoring double' (or more) for the length of a primary match which happened to be alongside that already found between the 'previous' two chains. A model equivalent to that of *Figure 3b*, (random chains and a 100 unit search), but with nucleation weighting of 2, is shown in *Figure 6* for compositions of $X_A=0.5$ and $X_A=0.75$. The weighting leads to a small reduction in $L(\%)$ as indicated in *Figure 7*.

Implications for crystallinity. The model demonstrates, in accord with the thinking of Flory[1-5], Wunderlich[7] and others[8-12], that crystallization of a random copolymer is conceivable, although the overall crystallinity will be low, especially when the chain composition is close to 50:50 and there is no searching. Nevertheless, if such crystallinity does occur above the glass transition it will provide crosslink points between the chains and would be sufficient to endow the material with the properties of a solid.

The model is two-dimensional, although it could be

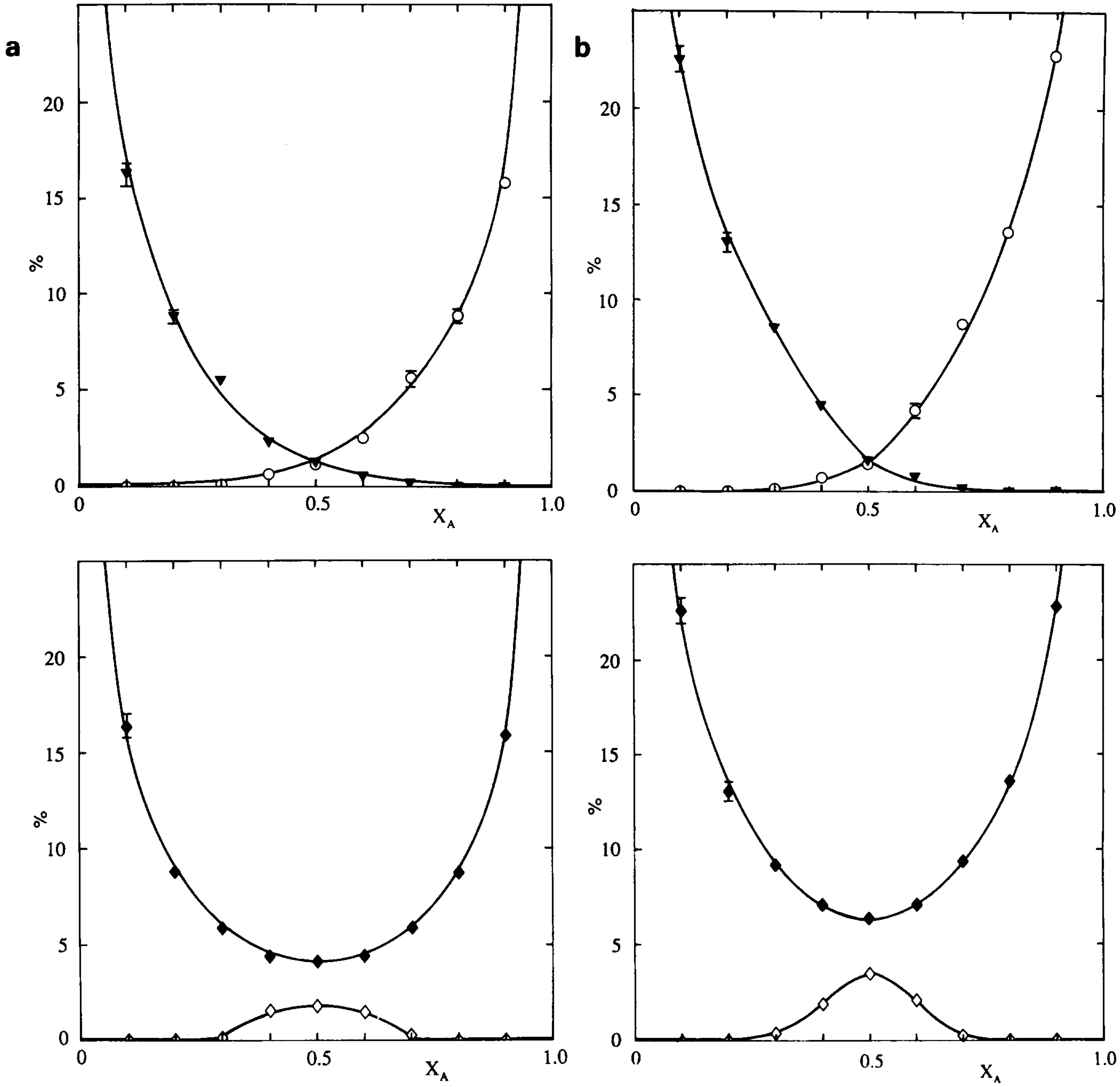

Figure 4 L_A% (○), L_B% (▼) (upper diagrams), L_{AB}% (◇) and L% (◆) (lower diagrams) *versus* X_A for ideal copolymer systems: (a) no search, and (b) a search of 100 units

designed to propagate in the third dimension as well. For the logic adopted, the chain organization predicted can be considered as being equivalent to sections through a three-dimensional model.

Chains with non-random dispositions of units. The parameter R'_P is unity for any ideal random chain, but tends to infinity for a full block copolymer, and to zero for an alternating polymer. In order to limit the number of variables, the effect of non-randomness in the chains is considered for only three compositions, $X_A = 0.5$, 0.75 and 0.9, for 100 unit searches and without a nucleation weighting. *Figure 8* shows the match density percentages as a function of $\log(R'_P)$ for the regular sequences described above. In *Figure 8a* only homopolymer matches were sought, in *Figure 8b* only alternating matches. *Figure 8c* shows the results of searching for the best regular match of either type. *Figure 9* compares the models for anti-blocky $R'_P = 0.2$ and blocky $R'_P = 5$ chains of composition $X_A = 0.5$, built with 100 unit searches, but no nucleation weighting. The pronounced effect of non-random statistics in encouraging the formation of ordered regions is clearly apparent.

Non-regular primary matches

An extension to the treatment of A, B and AB regular sequences above, leads to the possibility of assessing matches between non-periodic sequences. The lateral propagation of a particular non-periodic sequence would lead to a rather special type of crystallite in which there is three-dimensional organized packing and yet no periodicity along the chain axis. Such crystals have been discussed by Windle *et al.*[18] who referred to them as non-periodic layer (NPL) crystals (*Figure 10*). They were proposed to explain the lateral sharpness of meridional X-ray reflections, at positions characteristic of random sequences[19–21]. However, in this work, the question of

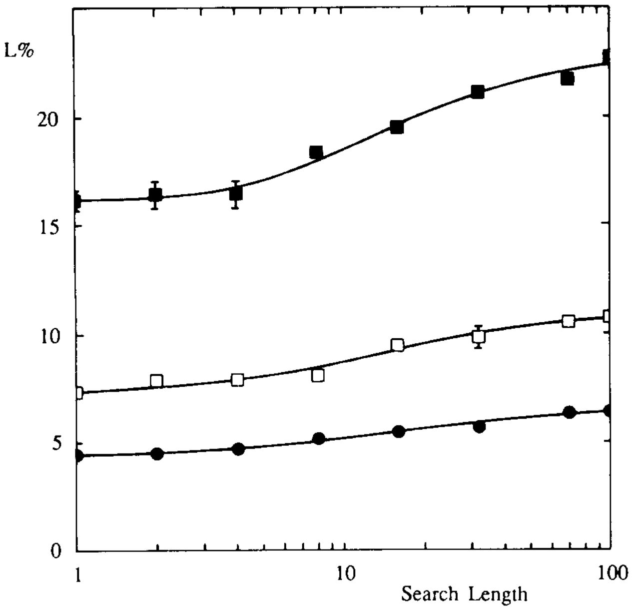

Figure 5 Effect of search length on primary homopolymer/AB regular match density ($L\%$): $X_A = 0.5$ (●), $X_A = 0.75$ (□) and $X_A = 0.9$ (■)

their thermodynamic stability is not addressed, for it is purely the geometric limits to NPL type matching which are explored, with particular reference to the influence of chain composition and blockiness.

Chain and match composition. The mean length of the primary NPL matches expressed as a percentage of the total chain length is shown as a function of chain composition in *Figure 11a*, for no searching and in *Figure 11b* for the 100 unit search. In each case the corresponding curves for the total regular sequence matches are shown as in *Figure 4*. It is clear that allowing the matches to be based on non-periodic sequences increases their probable length, especially in the mid-range of composition. *Figure 12* shows the composition of the matched sequences as a function of the overall compositions of the chains. It is particularly interesting that the match composition skews towards the dominant unit type. *Figure 13* shows NPL primary matches in 100 chain models with $X_A = 0.5$ for (a) no search, (b) 100 unit search and (c) 100 unit search with a nucleation weighting of 2.

Chain and match blockiness. Figure 14 is similar to *Figure 8c*, but plots match density against $\log(R'_P)$ for NPL rather than regular matches. As expected from the previous discussion, the NPL matches are longer than regular matches for the same chain composition. *Figure 15* examines the blockiness of the primary matches compared with the blockiness of the chains containing them. The blockiness of the matches appears to be more extreme than that of the chains, i.e. for $X_A = 0.5$, when $R_P < 1$ the matches tend to the anti-blocky extreme, whereas when $R_P > 1$ they tend to the blocky extreme. For $X_A = 0.75$ and 0.9, where the degree of anti-blockiness possible in the chain is limited (equation (9)), the matches tend only to the blocky extreme. The system is intrinsically biased so that the blockiest parts of the chains are the most likely to find a match. It is also for this reason that the match composition skews beyond the chain composition in the direction of the dominant unit.

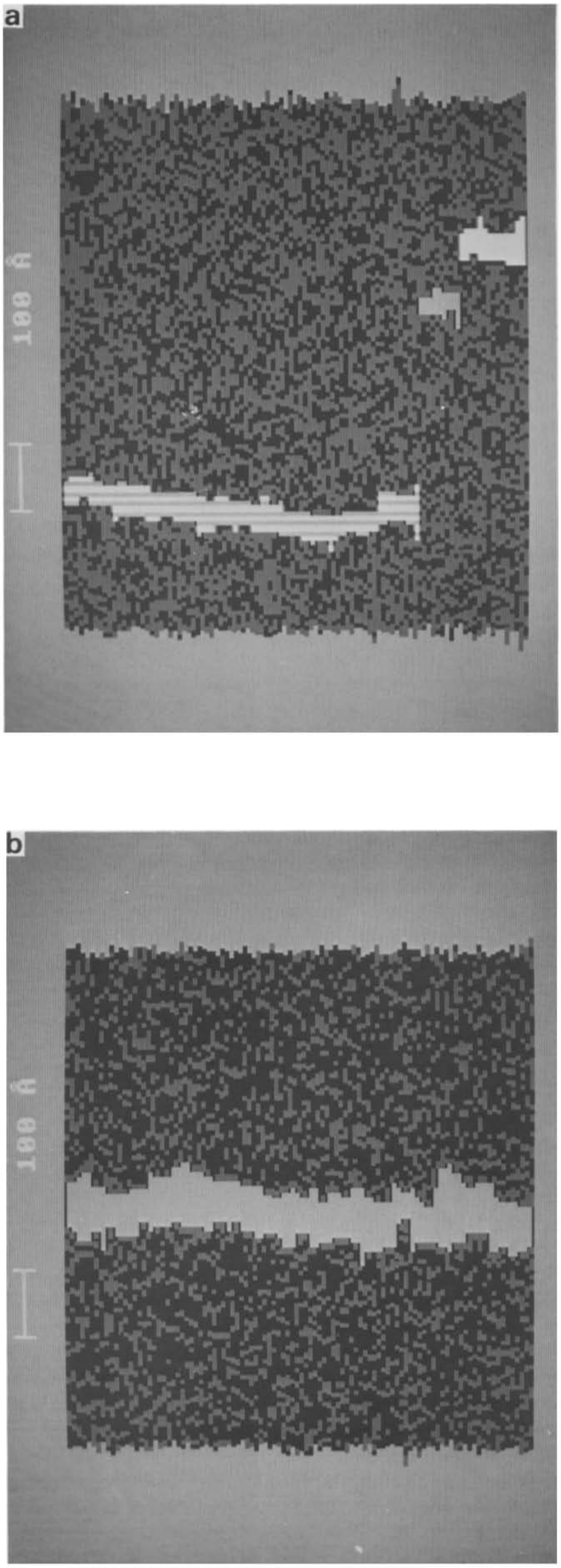

Figure 6 Plots of random copolymer systems showing homopolymer and AB regular primary matches for a search length of 100 units (full length) and a nucleation weighting of 2: (a) $X_A = 0.5$, (b) $X_A = 0.75$

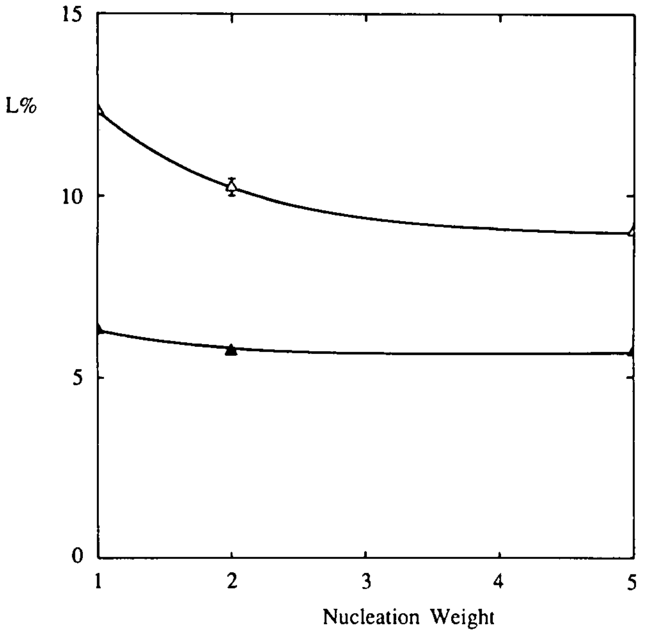

Figure 7 Primary match density ($L\%$) *versus* nucleation weighting for best regular matches (▲), and best match of any type (△), for random copolymer systems with composition $X_A = 0.5$, and a search length of 100 units (full length)

Secondary matches

So far only the best matching sequence between two adjacent chains has been considered. However, once this primary match sequence has been fixed, in general there exist a number of potential secondary matches between other parts of the chains. Secondary matches are defined as any matching sequence of any length. They are necessarily NPL sequences, since any two adjacent regular secondary matches will form one, longer, non-regular match. Whether or not a potential secondary match becomes an actual secondary match, depends on the two chains being in register at that point, which in turn depends on the relative lengths of units A and B, and the extent to which mis-registering will be allowed. In our model we consider all chains to be slightly elastic, and we define an axial variability parameter as the expected percentage variation in monomer unit length:

$$f \equiv \frac{\Delta l_i}{l_i} \times 100\% \qquad (14)$$

where l_i is the length of unit i. Further, we assume that f will apply equally well to a sequence of monomers of any length. The chains are considered to be pinned together at any match, and new secondary matches are accepted if their mis-register is less than $f\%$ of the distance, in Angstroms, to the nearest previous match. The variability parameter, f, represents the ability of a chain to extend or shorten itself, and can be expected to come within the range resulting from thermal motions.

Figure 16 shows a typical system containing both primary and secondary matches highlighted as described

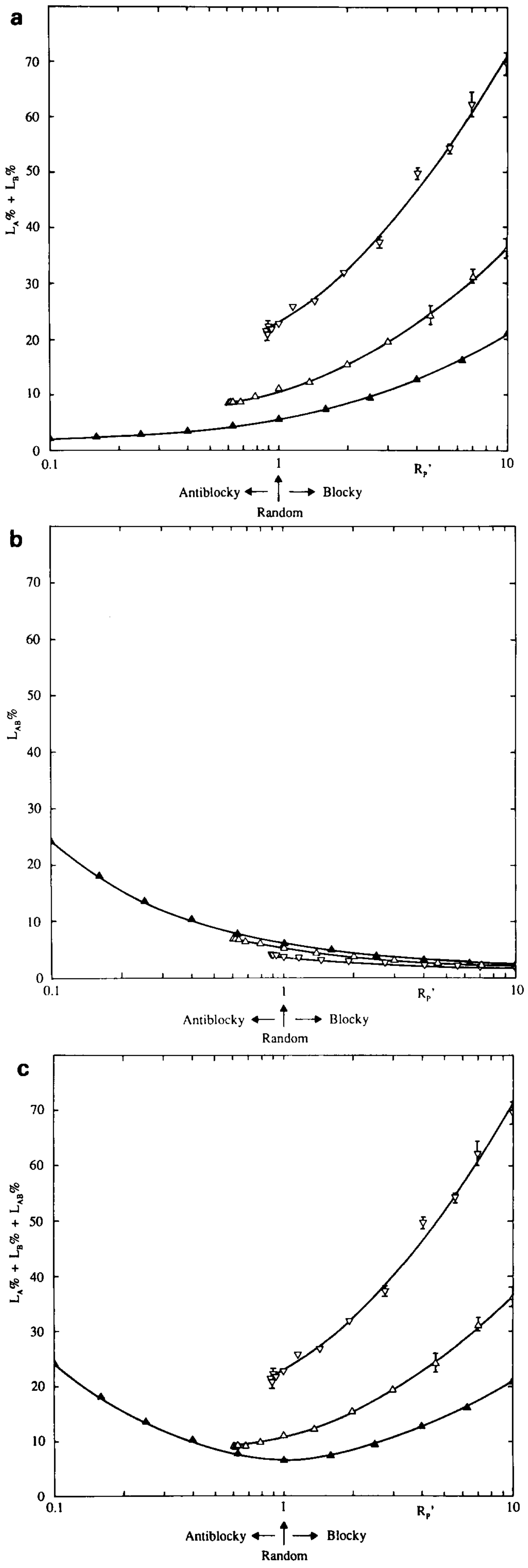

Figure 8 Primary match densities ($L\%$) are shown as a function of the blockiness parameter R_P' for $X_A = 0.5$ (▲), 0.75 (△) and 0.9 (▽). In (a) the density of pure homopolymer matches is shown, whereas (b) shows the density of AB regular matches; (c) shows the best primary match density, whether it be homopolymer or AB regular

above. A nucleation weighting of 5 was used to make the primary matches create a single ordered entity, and hence make it easier to see the secondary matches.

Variability in axial length. The effect of changing the axial variability parameter on mean match density is shown in *Figure 17* for NPL primary matches. As might be expected, increasing variability leads to more secondary matches. The graph shows both the normalized secondary match density, $S(\%)$, defined as the percentage of free chain (whole chain minus primary match) contained in secondary matches, and the total match density, $T(\%)$, defined as the percentage of chains involved in either primary or secondary matches. It is $T(\%)$ which represents the total crystallinity which might be seen. Energy calculations have shown that a suitable value for the variability parameter, at room temperature, is about 2% for poly(hydroxybenzoic acid), which leads to a crystallinity of 25% for NPL matches, for $X_A = 0.5$, which may be compared with a figure of 17% as measured by Blundell[22]. *Figure 18* shows how blocky chains enhance the total crystallinity, but reduce the secondary match density, $S(\%)$ for $f \leqslant 1\%$. This is seen as being due to blocky chains having fewer opportunities to come into register, for once a mis-register occurs it will be maintained if both chains consist of a long run of similar units and the axial variability is small.

Variation in monomer unit lengths. The effect of variation in monomer unit lengths is shown in *Figure 19*. In this figure, the length of unit A was fixed at 0.63 nm and the length of B varied. Peaks are observed in *Figure 19* at those points where the two unit lengths have common

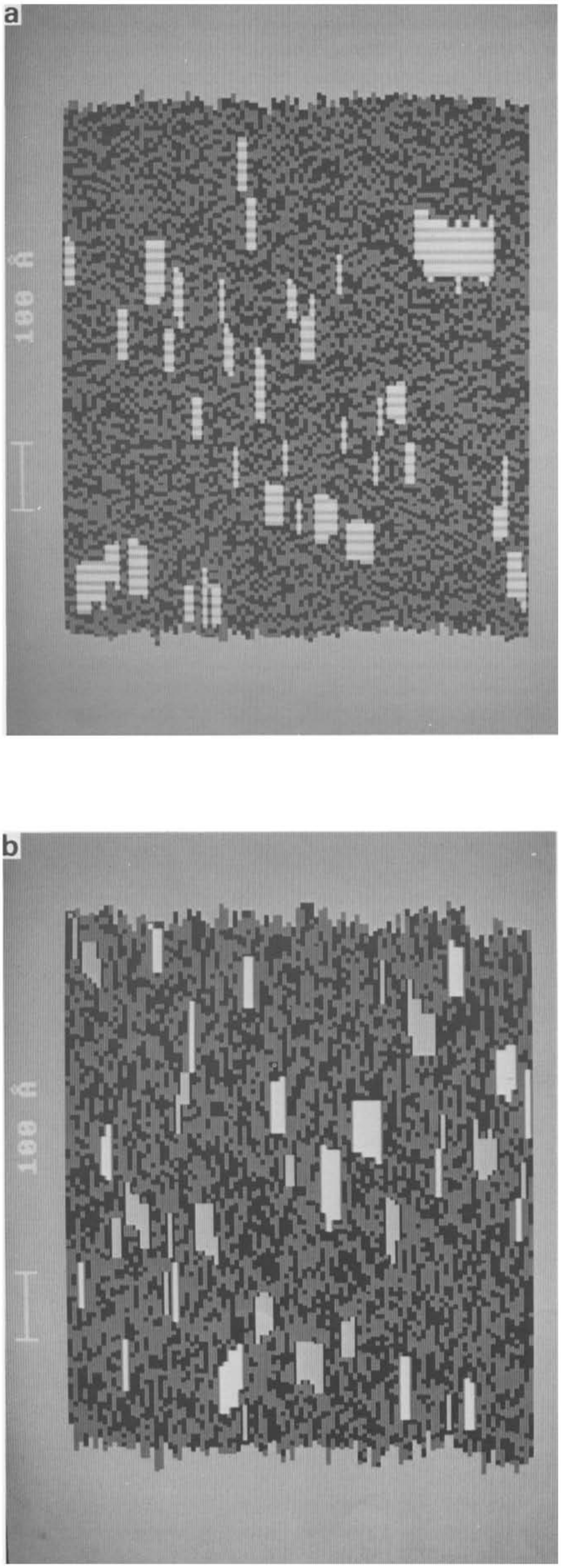

Figure 9 Plots of non-random copolymer systems, with $X_A = 0.5$, search length = 100 (full length) and no nucleation weighting: (a) $R'_P = 0.5$ (anti-blocky), (b) $R'_P = 2$ (blocky)

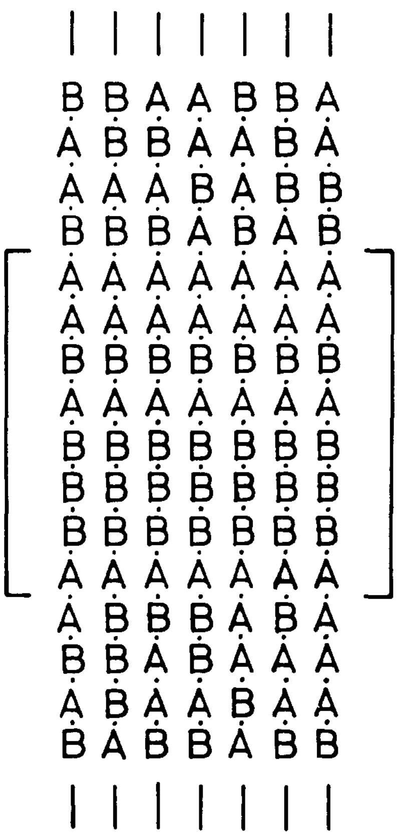

Figure 10 Several random copolymer chains, with units denoted by A and B, lined up so as to show a 'non periodic layer' (NPL) crystallite (Windle *et al.*[18])

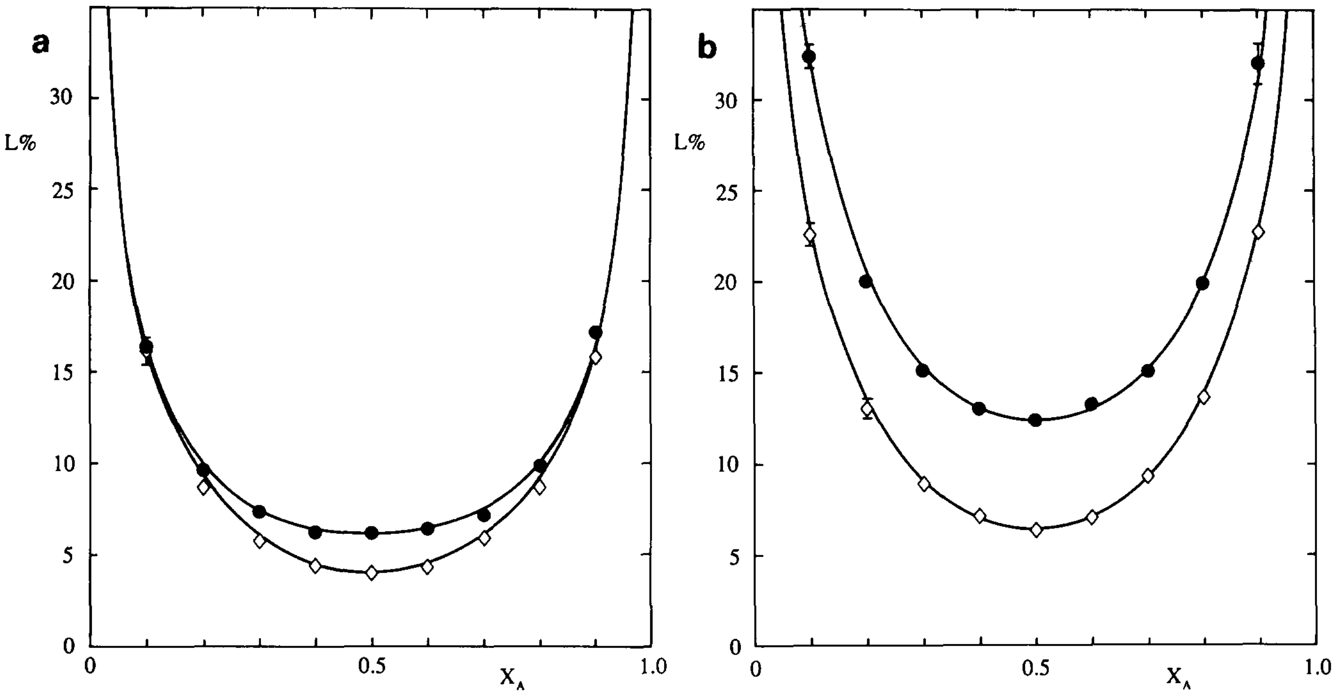

Figure 11 Primary NPL match density ($L\%$) *versus* X_A (●), for ideal copolymer system with no nucleation weighting: (a) search = 0, (b) search = 100 (full length). In each case the corresponding curve for regular matches (as in *Figure 4*) is also shown (◇)

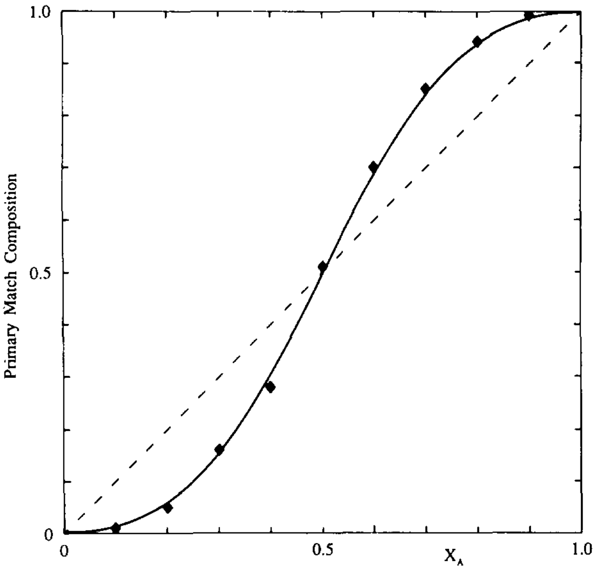

Figure 12 Composition of primary NPL matches as a function of X_A for random chains and search = 100. The points (◆) are results from Domino, while the smooth curve was generated using the theory from 'Statistical calculations' in the text

multiples, which bring the chains frequently into register, and the width of the peaks is determined by the variability parameter. The insert is a replot of the peak corresponding to the ratio 4:3 but calculated for a lower degree of axial variability. The peak is thus narrower, and small side peaks are now visible corresponding to ratios of 9:7 and 11:8.

STATISTICAL CALCULATIONS

The purpose of these calculations is to predict statistically the parameters describing some of the more straightforward models built by computer. In some respects, the mathematics is related to that already derived for homopolymer matches. We report a general equation which will give primary matching statistics for two component random copolymer chains, and has the flexibility to predict homopolymer matches (as has been done by Flory[4] and Wunderlich[7]) and matches between sequences which are not regular, such as those which contribute to NPL crystallites.

Sequence matches

Matches of NPL sequences. Consider two infinitely long adjacent chains, consisting of randomly arranged units A and B. If the probability of any unit being A is P_A, then the probability that the ith units of both chains match is:

$$r = P_A^2 + (1 - P_A)^2 \qquad (15)$$

If we look at any two adjacent sites, say i and $i+1$, the probability that both match will be r^2, and for a general sequence of n adjacent units, say i to $i+n-1$, the probability that the whole sequence matches the adjacent sequence may be written:

$$P(n) = r^n \qquad (16)$$

Since the above takes no account of whether the units immediately before and after the n unit sequence in one chain are also matched in the adjacent chain, we must interpret $P(n)$ as the probability that the sequence (units i to $i+n-1$) contains a match of length n units, or is part of a longer match. In order to restrict our probability to that of a match of length n units, and no longer, we multiply by the probability that the two adjacent units do not contain

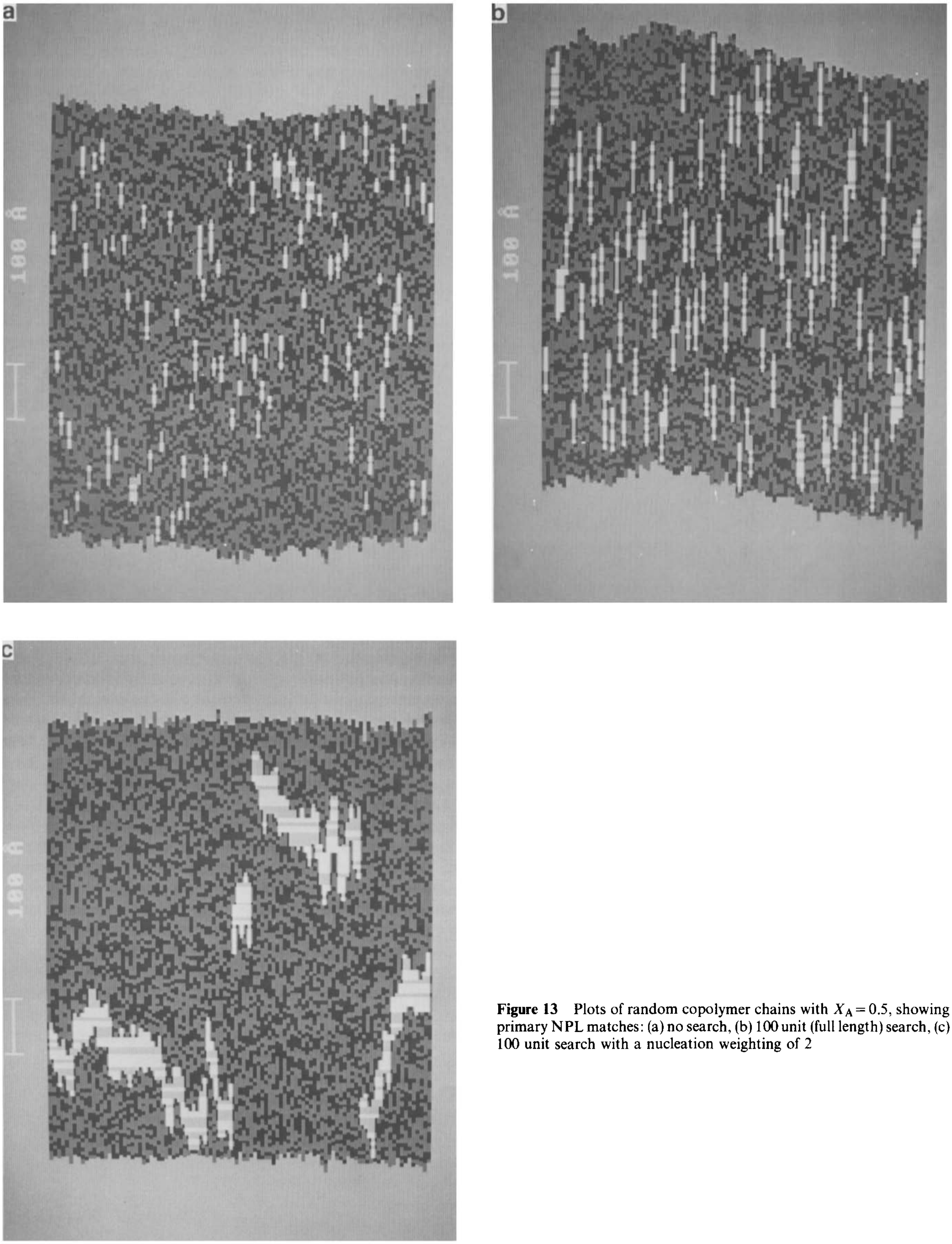

Figure 13 Plots of random copolymer chains with $X_A = 0.5$, showing primary NPL matches: (a) no search, (b) 100 unit (full length) search, (c) 100 unit search with a nucleation weighting of 2

a match, i.e. $(1-r)^2$, to give:

$$P'(n) = r^n \cdot (1-r)^2 \tag{17}$$

The binomial distribution may be written as:

$$D(a) = \binom{b}{a} \cdot P^a \cdot (1-P)^{b-a} \tag{18}$$

where

$$\binom{b}{a} = \frac{b!}{(b-a)!a!}$$

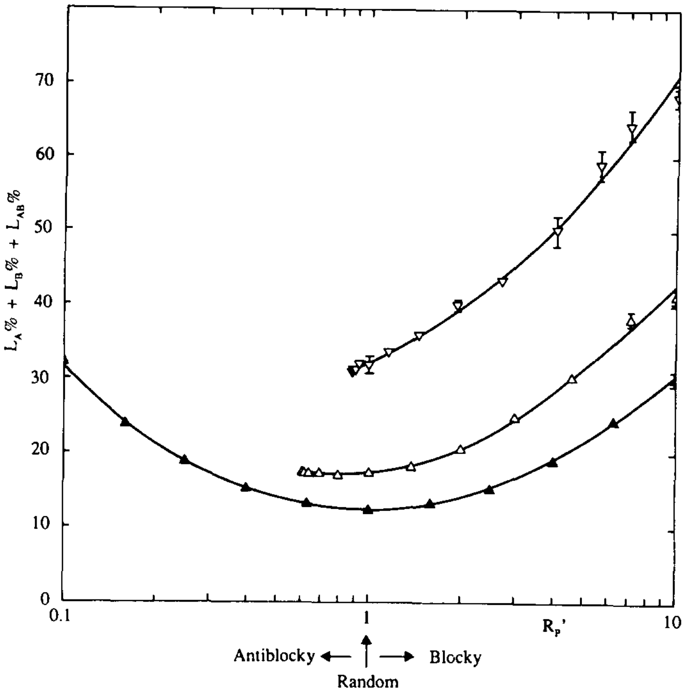

Figure 14 Primary NPL match densities ($L\%$) are shown as a function of the blockiness parameter R_P' for $X_A = 0.5$ (▲), 0.75 (△) and 0.9 (▽)

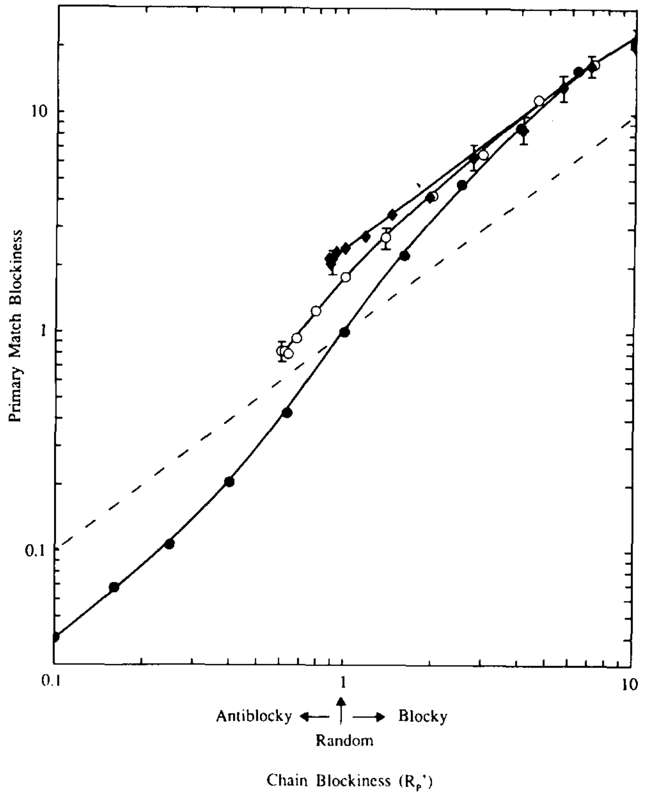

Figure 15 Blockiness ($R_P^{\text{Measured}}/R_P^{\text{Ideal}}$) of the NPL primary matches shown as a function of the chain blockiness R_P': $X_A = 0.5$ (●), $X_A = 0.75$ (○) and $X_A = 0.9$ (◆)

P is the probability of a success, and $D(a)$ gives the probability of a successes in b attempts. In our case we are interested in the probability of there being a success rather than a successes (!). This is best expressed as:

$$\text{Probability of a success} = 1 - D(0,n|m) \tag{19}$$

where $D(0,n|m)$ is the probability of there being no matches of length n in a chain of length m units.

Now, the best match distribution of Domino is given by the probability that there is at least one match of length n and that there are no matches longer. This is written as:

$$X_{\text{NPL}}(n|m) = [1 - D(0,n|m)]\cdot[D(0,n+1|m)\cdot D(0,n+2|m)\ldots$$
$$\ldots D(0,m-1|m\cdot D(0,m|m)] \tag{20}$$

i.e.

$$X_{\text{NPL}}(n|m) = [1 - (1 - P'(n))^{m-n+1}]\cdot \prod_{i=n+1}^{m} (1 - P'(i))^{m-i+1} \tag{21}$$

i.e.

$$X_{\text{NPL}}(n|m) = [1 - (1 - r^n\cdot(1-r)^2)^{m-n+1}]\cdot$$
$$\prod_{i=n+1}^{m} (1 - r^i\cdot(1-r)^2)^{m-i+1} \tag{22}$$

Figure 20 shows distributions of the best match lengths (curve I) calculated from equation (22), for $X_A = 0.5$, 0.75 and 0.9.

NPL match composition. It is possible to extend the expression for the probability of a match of length n:

$$P(n) = (P_A^2 + (1 - P_A)^2)^n \tag{15}$$

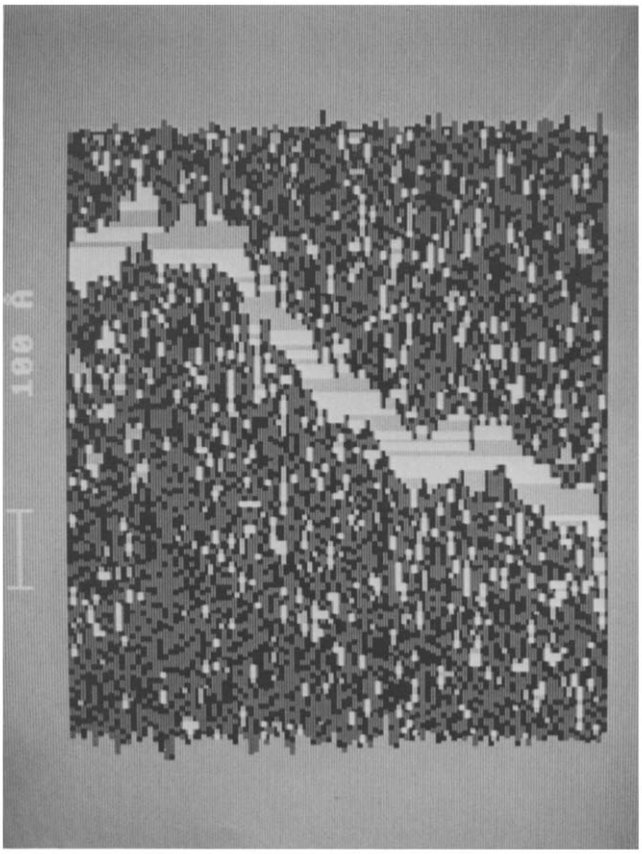

Figure 16 Plot of a random copolymer system with $X_A = 0.5$ and nucleation weighting = 5 showing both primary NPL matches and secondary matches. The high nucleation weighting ensures that it is easy to distinguish the primary matches as a continuous feature across the plot

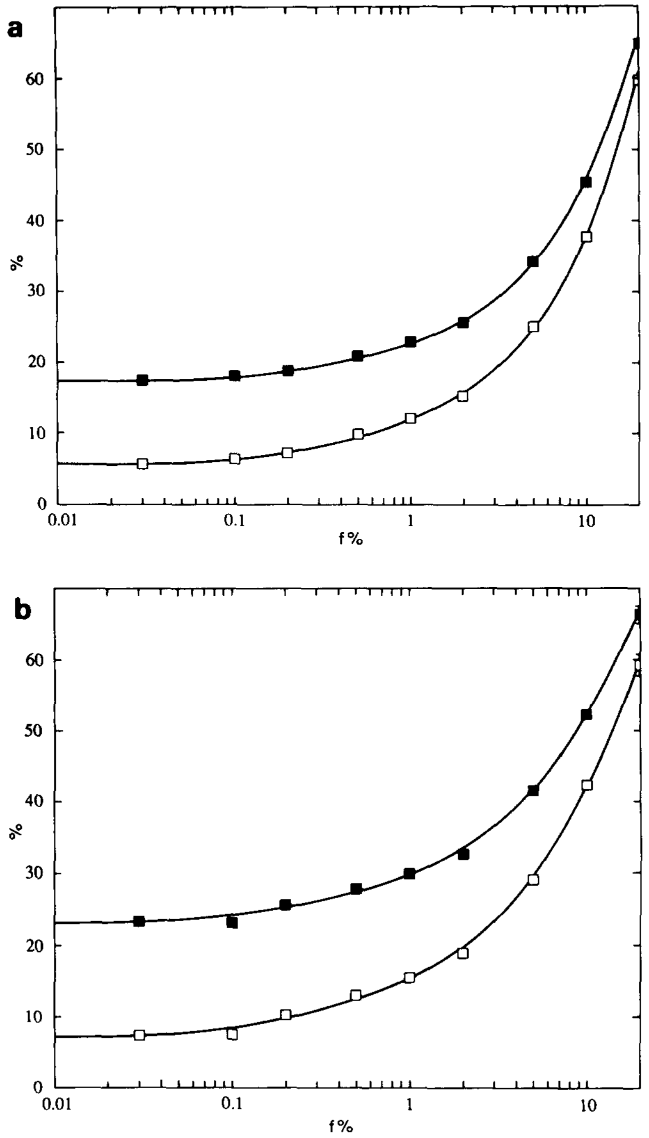

Figure 17 Total match density $T(\%)$ (■) and normalized secondary match density $S(\%)$ (□) plotted as a function of the flexibility parameter for random copolymer chains: (a) $X_A=0.5$ and (b) $X_A=0.75$. Unit lengths are 0.63 and 0.83 nm, respectively

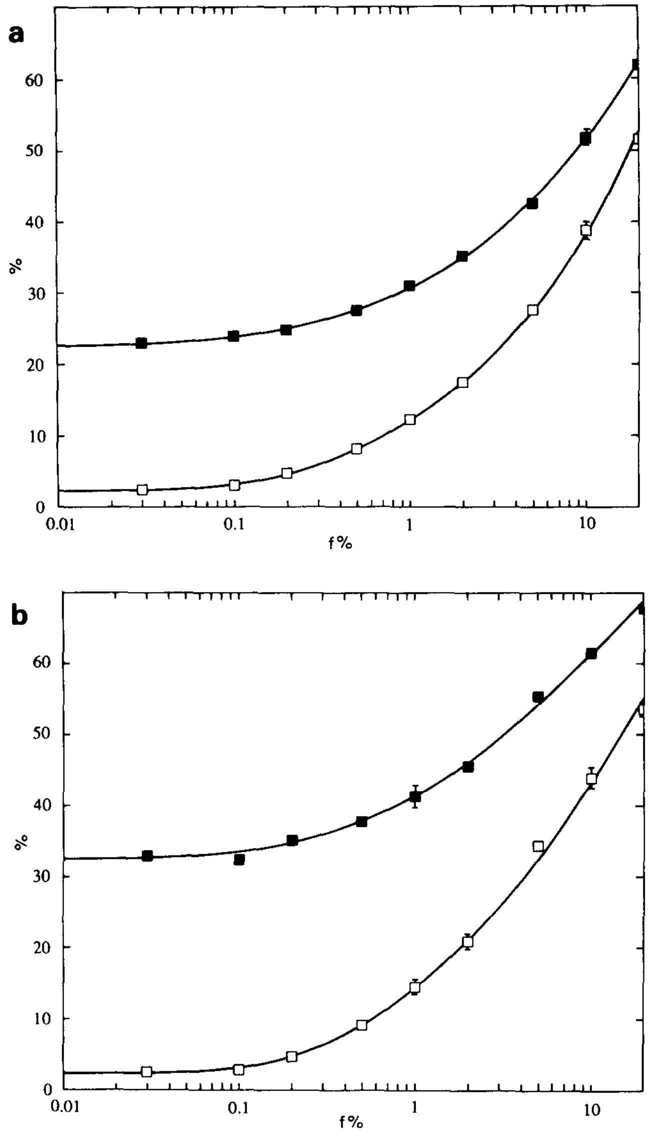

Figure 18 Total match density $T(\%)$ (■) and normalized secondary match density $S(\%)$ (□) plotted against the flexibility parameter for non-random chains ($R_P'=5$): (a) $X_A=0.5$ and (b) $X_A=0.75$. Unit lengths are 0.63 and 0.83 nm, respectively

to give the probability of a match of a given composition. Expanding the right hand side of equation (15) gives:

$$P(n)=\sum_{i=0}^{n}(n_i)\cdot(P_A^2)^i\cdot[(1-P_A)^2]^{n-i} \qquad (23)$$

or

$$P(n)=\sum_{i=0}^{n}P(i|n) \qquad (24)$$

$P(i|n)$ represents the probability of a match of length n, containing i units of type A. Thus the average composition of matches of length n may be computed from:

$$\langle i\rangle=\frac{\sum_{i=0}^{n} i\cdot P(i|n)}{P(n)} \qquad (25)$$

for a given value of P_A. The mean match composition so

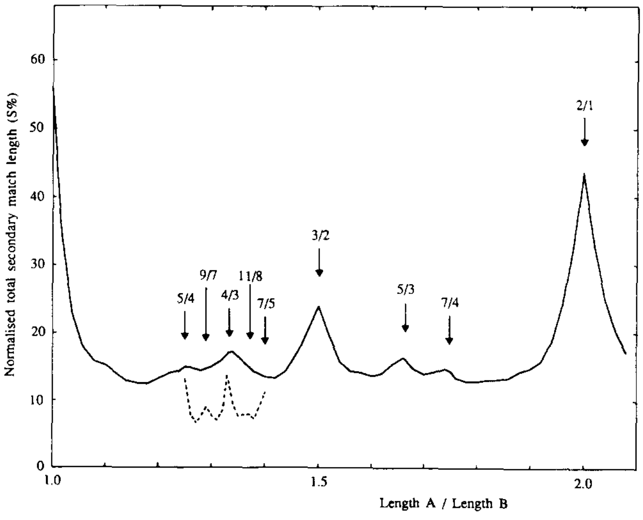

Figure 19 Effect of variation in monomer length on secondary match density with X_A for ideal chains and variability parameters of $f=1\%$ (———) and (inset) $f=0.1\%$ (– – –)

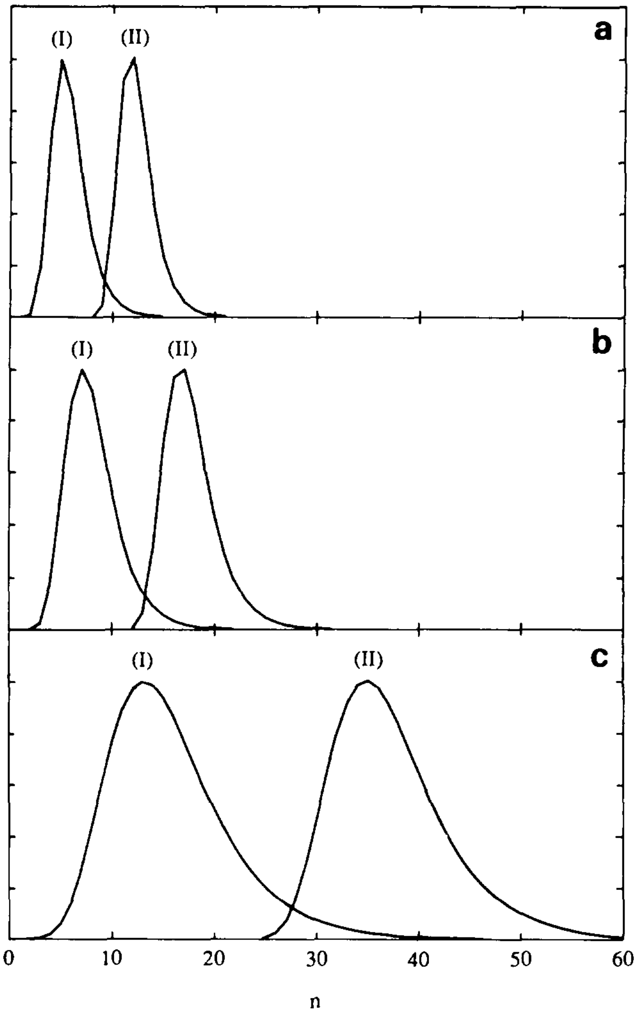

Figure 20 Calculated match length distributions for NPL primary matches for compositions of (a) 0.5, (b) 0.75 and (c) 0.9: (I) quenched, and (II) annealed systems

derived is shown in *Figure 12* (continuous curve), in comparison with the measured match compositions from Domino for quenched systems. The prediction of skewing of match composition is good.

Homopolymer matches. The treatment is similar to the NPL case. The basic probability with which we are concerned is the probability of either an n unit homopolymer match of type A, or an n unit homopolymer match of type B. Hence if we put:

$$s = P_{\mathrm{A}}^2 \quad ; \qquad t = (1 - P_{\mathrm{A}})^2 \tag{26}$$

then

$$P(n) = s^n + t^n \tag{27}$$

and

$$P'(n) = s^n \cdot (1-s)^2 + t^n \cdot (1-t)^2 \tag{28}$$

Thus, substituting into equation (21), we obtain:

$$\mathrm{X}_{\mathrm{Homo}}(n|m) = \left[1 - (1 - s^n \cdot (1-s)^2 - t^n \cdot (1-t)^2)^{m-n+1}\right] \cdot \prod_{i=n+1}^{m} (1 - s^i \cdot (1-s)^2 - t^i \cdot (1-t)^2)^{m-i+1} \tag{29}$$

Examples of the distribution of best homopolymer match lengths (curve II) are shown in *Figure 21*.

Searched matching. In the searching process, one chain is held fixed while the other is cycled past it. This means that, for chains of length m, we have $(m-n+1) \cdot m$ attempts at finding a match of length n, and equations (22) and (29) become:

$$\mathrm{X}_{\mathrm{NPL}}^{\mathrm{Search}}(n|m) = \left[1 - (1 - r^n \cdot (1-r)^2)^{(m-n+1) \cdot m}\right] \cdot \prod_{i=n+1}^{m} (1 - r^i \cdot (1-r)^2)^{(m-i+1) \cdot m} \tag{30}$$

and

$$\mathrm{X}_{\mathrm{Homo}}^{\mathrm{Search}}(n|m) = \left[1 - (1 - s^n \cdot (1-s)^2 - t^n \cdot (1-t)^2)^{(m-n+1) \cdot m}\right] \cdot \prod_{i=n+1}^{m} (1 - s^i \cdot (1-s)^2 - t^i \cdot (1-t)^2)^{(m-i+1) \cdot m} \tag{31}$$

respectively (see *Figures 20* and *21*, curves (II)).

Effect of chain length on match length. A final application of equation (22) is to demonstrate the effect of chain length on match length, and hence percentage crystallinity. We consider the quenched NPL case, for three compositions. Results are shown in *Figures 22* and *23*. Whilst shorter chains naturally contain shorter matches, the proportion of chain involved in the matches

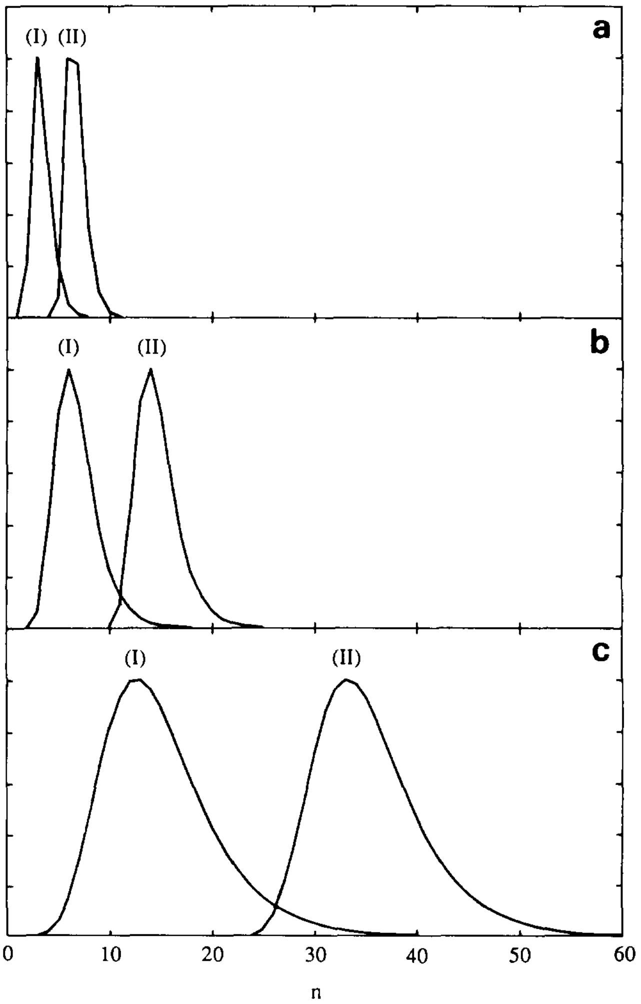

Figure 21 Calculated match length distributions for homopolymer primary matches for compositions of (a) 0.5, (b) 0.75 and (c) 0.9: (I) quenched, and (II) annealed systems

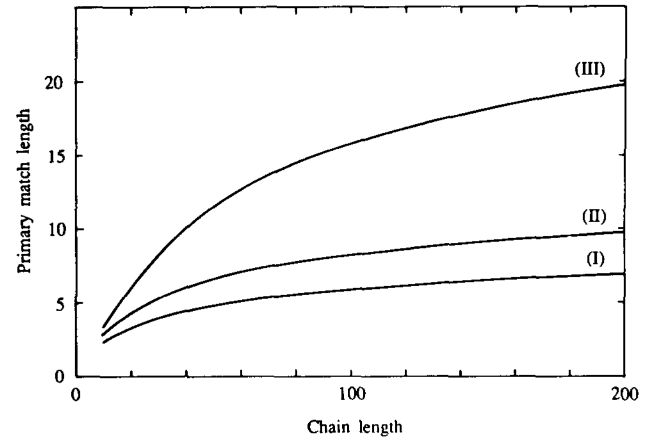

Figure 22 Calculated primary NPL match length as a function of chain length for chains of composition (I) 0.5, (II) 0.75 and (III) 0.9, using equation (22) (quenched chains)

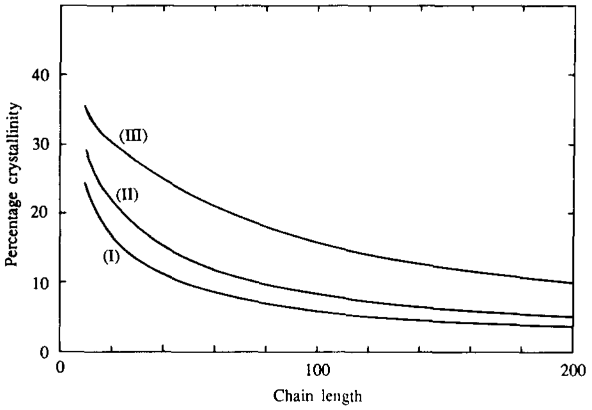

Figure 23 Calculated primary NPL match crystallinity as a function of chain length for chains of composition (I) 0.5, (II) 0.75 and (III) 0.9 for quenched chains

actually increases, hence the percentage crystallinity increases.

Comparison between Domino and statistical theory

Table 1 contains mean values for the match length distributions generated by Domino and the statistical theory, for comparison. The agreement is good when $P_A = 0.5$, and in all the quenched cases. However, Domino falls short of the predicted matching in the searched cases for $P_A \neq 0.5$, especially in the case of homopolymer matches.

We have investigated this lack of agreement, and have concluded that the problem lies in our use of the Binomial distribution in calculating $X(n|m)$. When we discuss the number of attempts we may have at finding a match between two chains (i.e. the number of positions where we may look) we are assuming that each attempt is independent of all others. In the quenched case, provided we have ideal random chains, this appears reasonable. In the searched case, the problem is most easily visualized by considering homopolymer matches for chains with composition $P_A = 0.9$. The best match between two such chains is automatically restricted by the longest homopolymer runs in the two chains, and will be equal to the shorter of the two. If, instead of cycling the second chain through *m* positions, we generate *m* independent chains, and take the chain which matches best to the first without cycling, we obtain a very different answer. Referring to *Table 1*, and considering again the case for homopolymer matches and a chain composition of 0.9, we are looking for an average best match length of 35.7 units, while Domino gave 22.7 units. We obtain by this new method of searching in Domino, an average best match length of 48.5 units for chains of length 100 units. We can see that we are in fact searching for a match which is at least as long as the longest homopolymer sequence on the fixed chain. So keeping the same fixed chain for *m* different matching chains does not actually produce independent matching. The only way to have independence is to consider *m* pairs of chains, and to look for the best match from this ensemble. Each pair of chains is assumed quenched, and the result we obtain for the average best match length is 36.5 units. This may bring the computer model in line with the mathematical one, but it also emphasizes the lack of realism of this particular solution, and we do not develop it further.

Thus in general, the analysis as developed is invalid for searched chains, although the difficulty is only apparent for chains in which one type of unit predominates. Indeed, as we approach $P_A = 0.5$, the closeness of the agreement would seem to imply that the independence criterion is being met.

RELATION TO EXPERIMENT

The computer modelling and statistical calculations above were stimulated by a series of experimental data obtained from random copolyesters such as that shown in *Figure 1*. The data fall into three classes:

1. Differential scanning calorimetry (d.s.c.) of the melting process.
2. X-ray diffraction analysis.
3. Transmission electron microscopy.

The development of thermotropic random copolyesters based on molecules without side groups has been driven by the objective of making stronger, stiffer and more thermally stable thermoplastics which can be either moulded in conventional equipment or drawn into fibres. Assessed mechanically, the copolymers appear to melt within a comparatively narrow temperature range around 300°C, although intriguingly, under conditions of continued shear, there is some indication that flow can be maintained at temperatures below the melting point[23]. Thermal analysis by d.s.c. also shows a clear melting endotherm, however the background, especially at temperatures below melting, appeared at first to be uneven and irreproducible. It has been shown[18]

Table 1 A comparison of mean primary match lengths for the Domino computer model, with those predicted by the statistical equation derived in the text

		Homopolymer matches		NPL matches	
		Domino	Theory	Domino	Theory
$X_A = 0.5$	Quenched	4.05	3.51	6.25	5.88
	Searched	6.40	6.80	12.73	12.42
$X_A = 0.75$	Quenched	7.05	6.93	8.03	8.23
	Searched	11.15	14.78	17.07	17.79
$X_A = 0.9$	Quenched	15.85	15.20	17.90	15.84
	Searched	22.75	35.67	31.20	37.45

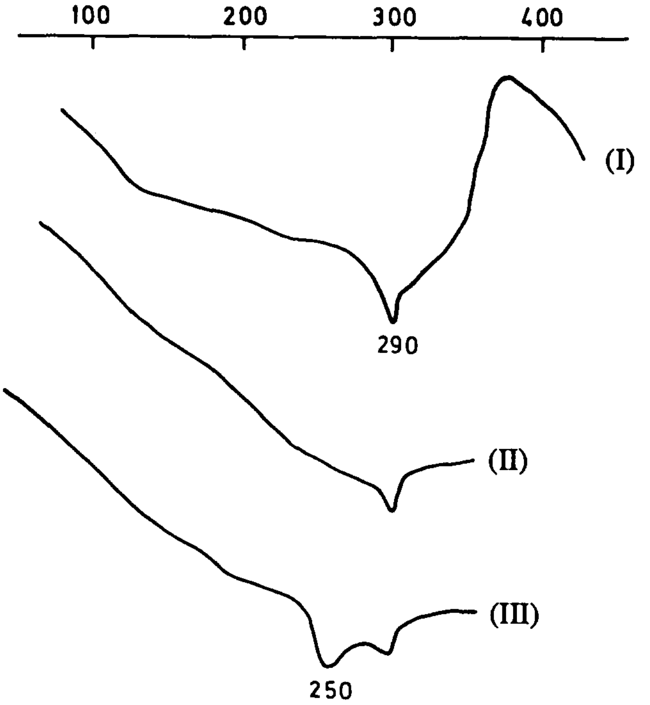

Figure 24 Thermal analysis traces for a copolymer of hydroxybenzoic and hydroxynaphthoic acids (B–N), with a heating rate of 30°C min^{-1}: (I) as received, (II) after quenching from 320°C and (III) after annealing at 220°C. Peak temperatures in degrees Centigrade (Windle *et al.*[18]). [Reproduced from Windle, A. H., Viney, C., Golombok, R., Donald, A. M. and Mitchell, G. R. *Faraday Discuss. Chem. Soc.* 1985, **79**, paper 5 by permission of the Royal Society of Chemistry ©]

that a possible interpretation of the 'background' is in terms of a very broad premelting endotherm. Annealing treatments up to 100°C below the melting point leave their mark as localized deviations on subsequent thermal analysis plots. This behaviour is shown in *Figure 24*[18]. The evidence thus points to a reasonably well defined melting phenomenon with the physical liquification of the polymer correlating with a distinct endotherm. In addition, there is a considerable temperature range over which a measure of premelting seems to occur, such as was predicted by Flory[2,4].

The sharpness of wide angle diffraction maxima from thermotropic random copolymers would be indicative of some measure of crystalline order, and this is lost above the main melting transition, where the main intermolecular peak broadens as it becomes characteristic of a nematic liquid phase (*Figure 25*)[18]. The order is also apparent in diffraction patterns of fibre samples. Where these are annealed close to the melting point there is a clear sharpening of the diffraction peaks, and the development of a series of sharp but weak reflections which, for polymers with hydroxybenzoic acid as the major component, correspond to the diffraction pattern reported for the corresponding homopolymer[24]. The diffraction evidence thus points to a dominant ordered component which is not purely a homopolymer. Most of the diffraction intensity is concentrated into a single equatorial maximum and the meridional reflections. These latter, while comparatively sharp with little spreading along the layer lines, are at spacings consistent with a random copolymer chain[19,20].

It should perhaps be recorded that the idea of NPL crystallites[18] stemmed from consideration of the available X-ray data, and the subsequent modelling reported above has demonstrated the extent to which this type of order could pervade the material under a range of conditions.

Transmission electron microscopy of thin films of random copolyesters can show, under suitable conditions, contrast effects which indicate the presence of small ordered entities. It was found[25] that the entities became visible in samples of copolyesters, such as that of *Figure 1*, which had been annealed on a rock salt substrate at a temperature about 100°C below the melting point. The entities were only visible in dark field, and were clearest when the diffraction aperture was in the region of the equatorial reflection. Some can be seen in the micrograph[18] of *Figure 26*. In some cases the entities were elongated normal to the direction of chain orientation induced by shearing the specimen. If the sizes observed are taken to be an upper limit, especially with regard to thickness in the chain direction where projection effects are likely to exaggerate the dimension, the scale of the

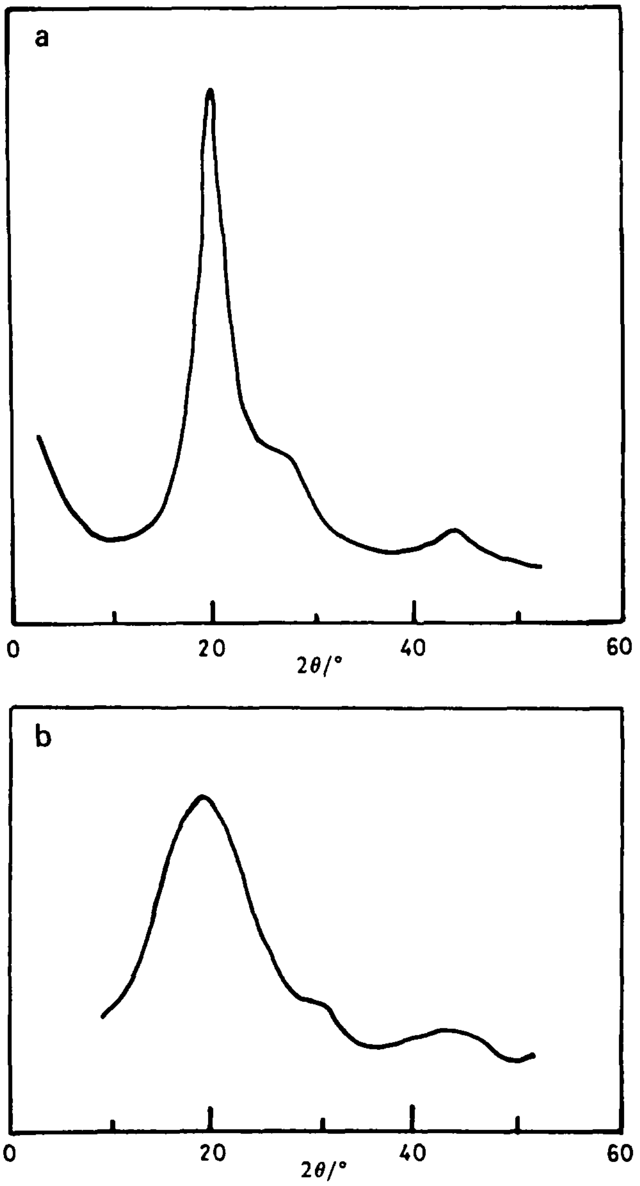

Figure 25 X-ray diffractometer scans of an unoriented sample of B–N at: (a) 20 and (b) 300°C (Windle *et al.*[18]). [Reproduced from Windle, A. H., Viney, C., Golombok, R., Donald, A. M. and Mitchell, G. R. *Faraday Discuss. Chem. Soc.* 1985, **79**, paper 5 by permission of the Royal Society of Chemistry ©]

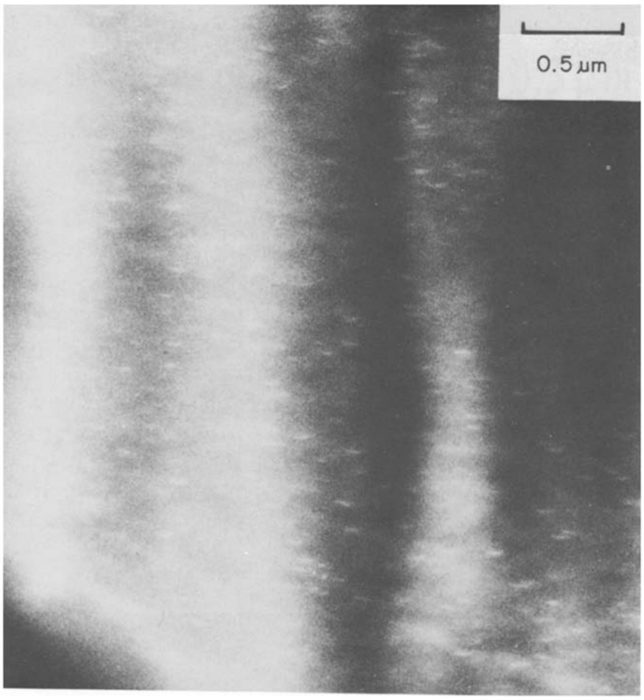

Figure 26 Dark field micrograph of B–N sheared and then annealed for 20 min at 200°C showing small but strongly scattering entities. The shear axis is vertical (Windle *et al.*[18]). [Reproduced from Windle, A. H., Viney, C., Golombok, R., Donald, A. M. and Mitchell, G. R. *Faraday Discuss. Chem. Soc.* 1985, **79**, paper 5 by permission of the Royal Society of Chemistry ©]

entities, ~20 nm thick and ~100 nm long, it is not inconsistent with the predictions of the modelling above, especially where a measure of nucleation weighting is included.

CONCLUSIONS

The aim of the work described here, has been to investigate the geometrical limits to order in random copolymers, with a view to determining the effect of various chain and match parameters. We conclude:

(1) The mean length of both NPL and homopolymer primary matches increases as the chain composition changes from $X_A = 0.5$ to $X_A = 1$ or $X_A = 0$.

(2) When $X_A \neq 0.5$, the composition of NPL matches is biased towards the dominant component.

(3) The mean primary match length increases when the chains are cycled past each other in a searching routine to find the best match. In the case of NPL matches, searching over 100 units leads to an approximate doubling of primary match length.

(4) When chains are built with pronounced non-random statistics, the mean primary match lengths increase.

(5) The primary matches between non-random chains show a more pronounced degree of non-randomness than the chains themselves, i.e. blocky chains contain blockier matches.

(6) The number of secondary matches increases as the chain composition changes from $X_A = 0.5$ to $X_A = 1$ or $X_A = 0$.

(7) When the axial variability parameter exceeds 1%, the number of secondary matches is approximately independent of chain blockiness. When the variability is less than 1%, the number of secondary matches decreases as the blockiness increases.

(8) For given chain parameters, the number of secondary matches will be determined by the percentage difference in length of the monomer units relative to the size of the axial variability parameter used. For unit lengths of simple ratio the number of secondary matches is enhanced.

(9) The degree of crystallinity (i.e. the volume of matches divided by the volume of chains) increases as the chain length decreases.

ACKNOWLEDGEMENTS

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