# Crystallisation in polymer films: control of morphology and kinetics of an organic dye in a polysilicone matrix

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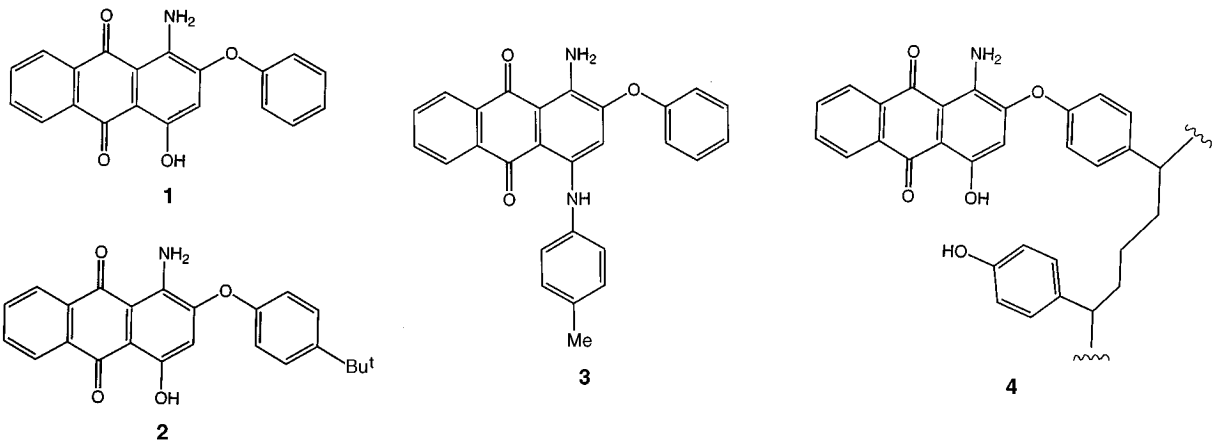
The successful selection, design and synthesis of additives for the control of nucleation and crystallisation of a red anthraquinone based dye is described. This procedure is based on the crystal structure and morphology of solution grown crystals and in this study the possibility of using the same approach to control crystallisation within an amorphous polymeric matrix is explored. The work has been motivated by the desire to prepare stable dye sheets for thermal transfer printing applications, yet the parallel with natural biomineralisation processes is clear.

Recent years have seen significant advances in the understanding of structural mechanisms available for the control of crystallisation processes.[1–3] Thus, the factors leading to the design of auxiliary molecules for the control of nucleation and growth of both organic and inorganic materials are now well understood.[4,5] One area of particular interest, largely in the context of materials design, has been biomineralisation. Here, biological systems are seen as models for the expression of highly organised structures comprising simple inorganic crystals located in macromolecular matrices (*e.g.* calcium phosphate in collagen). A number of studies have already been reported which attempt to mimic these processes using synthetic polymers as matrices in which simple inorganic species are nucleated and grown.[6,7] In this study we present for the first time an example of an organic molecule crystallising within a polymer film and show how the existing strategies for the control of crystallisation from solutions and melts can be successfully transferred to crystallisation from an amorphous polymeric matrix. The work was motivated by the commercial need to develop dye sheets for use in thermal transfer colour printing,[8–10] in which the dye was stabilised against crystallisation during storage.

## Experimental

The dye chosen for this work was the red, anthraquinone-based 1-amino-4-hydroxy-2-phenoxyanthraquinone **1**, supplied by ICI. Crystallisation was carried out both from solutions in butanone and from films comprising crosslinked polydimethylsiloxane, also supplied by ICI. These films were prepared by coating a solution of dye, polymer, crosslinker and catalyst (dibutyltin) in $CH_2Cl_2$ onto a 6 μm melinex support [biaxially oriented poly(ethylene terephthalate)] using a K-bar (R K Print-Coat Instruments Ltd.) to give coatings 24–54 μm in thickness. After spreading, the solvent was evaporated using a hot air drier and the film cured at 100 °C for 30 s to complete the crosslinking. This left a final film of *ca.* 1 μm thickness. By carrying out the final cure for variable times and on a microscope hot stage, the nucleation and growth of dye crystals at 100 °C in these initially amorphous films was monitored. Dye concentrations in the original solutions were chosen to be 0.28, 0.56 and 0.85 wt.% and each measurement reported is the mean of seven experiments.

Crystals of the dye were grown from solution by slow evaporation of 1% butanone solutions at 30 °C. Owing to the



colour intensity of such solutions it was not possible to monitor the progress of these experiments. When only a little solvent remained the solutions were filtered and the crystals examined by SEM. Crystals grown from pure solutions were examined by optical microscopy and optical goniometry in order to define their morphology. The theoretical morphology was calculated using the program HABIT[3] and the potentials of Momany *et al.*[11]

Small molecule additives [1-amino-2-(4-*tert*-butylphenoxy)-4-hydroxyanthraquinone **2** and 1-amino-2-phenoxy-4-toluidinoanthraquinone **3**] were supplied by ICI. These materials were characterised by NMR spectroscopy, thin layer chromatography (TLC) and microanalysis and found to have purities in excess of 98%. The polymeric additives were the products of grafting 1-amino-2-bromo-4-hydroxyanthraquinone onto copolymers of styrene and vinylphenol (**4**). Poly(vinylphenol)s of varying vinylphenol contents were synthesised by reacting vinylphenol (prepared by the method of Hatakeyama *et al.*[12]) (0.044, 0.11, and 0.15 mole fraction) with styrene at 60 °C for 50 h using azoisobutyronitrile (AIBN) as an initiator. The copolymers were recovered by dissolving the reaction mixture in butanone and precipitating the polymer with MeOH. 1-Amino-2-bromo-4-hydroxyanthraquinone was then grafted onto these polymers by reaction in *N*-methylpyrrolidone at 135 °C for 20 h. The resultant grafted polymers were recovered by precipitation with MeOH. Characterisation was performed by gel permeation chromatography (GPC), to measure the molecular weight relative to a polystyrene standard, and proton NMR, FTIR and UV–VIS spectroscopy to assess the extent of grafting.

For subsequent solution growth experiments additives were added at levels of 1 wt.% on dye, while in the polymer films levels up to 15 wt.% on dye were used.

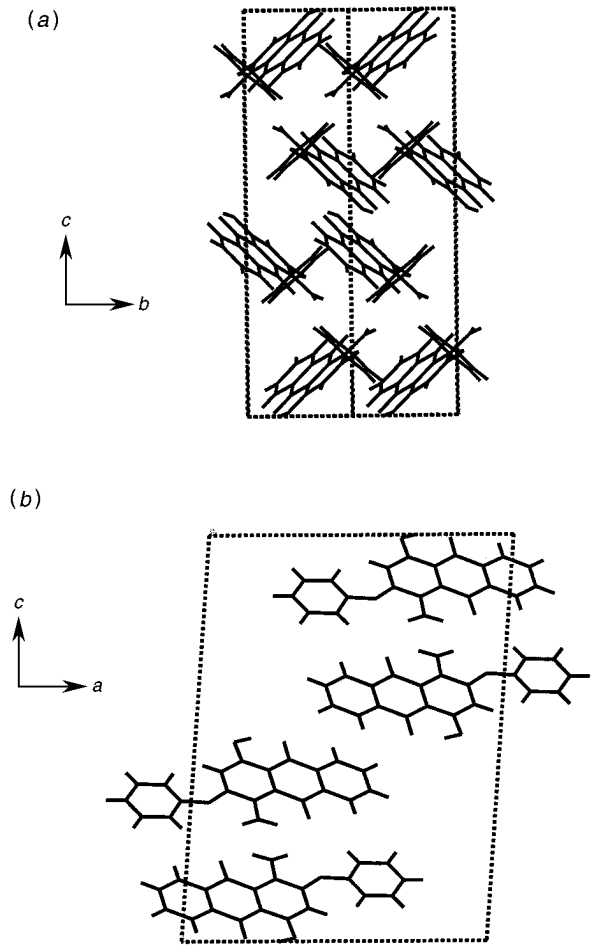



**Fig. 1** The crystal structure of **1** (*a*) viewed down [100], and (*b*) viewed down [010]

## Crystal structure and additive design

The crystal structure of the dye used here has been reported previously.[10] It belongs to the monoclinic space group $P2_1/c$ with four molecules in the unit cell and $a=1.4972$, $b=0.5141$ and $c=1.9853$ nm and $\beta=94.15°$. The anthraquinone and phenoxy rings adopt a dihedral angle of 97° and the molecules are held in the structure by van der Waals and $\pi$–$\pi$ interactions. There are no intermolecular hydrogen bonds. Fig. 1(*a*) viewed down the *a*-axis shows the herringbone motif and indicates that the $\pi$–$\pi$ interactions lie along [010]. Fig. 1(*b*) is a view down the *b*-axis. Fig. 2(*a*) is a scanning electron micrograph of solution grown crystals which adopt a needle morphology in which the needle axis corresponds to [010] with large {101} and smaller {101} and {002} side faces, as determined by optical goniometry. The predicted morphology is shown in Fig. 2(*b*) and is in reasonable agreement with experiment with elongation along [010] as expected from the $\pi$–$\pi$ interactions, with {002}, {200} and {101} as the most important side faces.

The overall objective of this study was to prevent crystallisation of dye molecules within the polymeric films by including in the formulations additives which would inhibit nucleation and growth of crystals. It was on the basis of the above structural and morphological data that such additives were selected and designed as molecules likely to inhibit crystallisation of specific faces of the dye crystals. For example, in the {101} faces molecules present either their phenoxy or their anthraquinone rings to the growth environment [Fig. 1(*b*)]. Hence substitution at the *para* position on the phenoxy ring by a bulky group should yield a molecule that is recognised by the crystal surface but which, once in position, will sterically

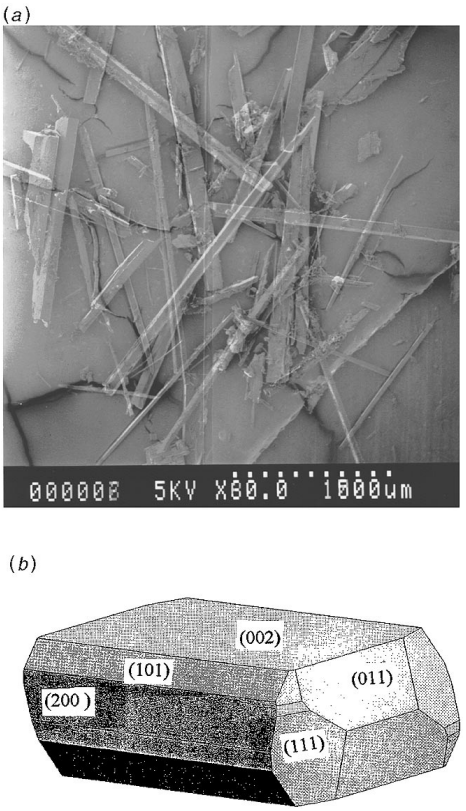



**Fig. 2** The morphology of 1-amino-4-hydroxy-2-phenoxyanthraquinone crystals: (*a*) solution grown and (*b*) predicted from the crystal structure

prevent addition of further molecules to the growing crystal. For {020} there are four different molecular orientations [Fig. 1(*a*)], however in two of these the hydroxy group is directed away from the surface such that its replacement by a bulkier substituent might be expected to inhibit growth in this direction. Bearing these conclusions in mind two potential additives were selected, one in which the phenoxy ring was substituted at the *para* position by a *tert*-butyl group (**2**) and was designed to inhibit growth on the (101) face, and a second in which the hydroxy group was replaced by a toluidino group (**3**) designed to inhibit (020). Their likely positions in the two surfaces are shown in Fig. 3(*a*) and (*b*). In addition, the polymeric additives (**4**) described above were synthesised with the aim of providing the possibility of multidentate binding to the surfaces to compare with the small unidentate molecules. This is shown schematically in Fig. 3(*c*) for the {101} faces.

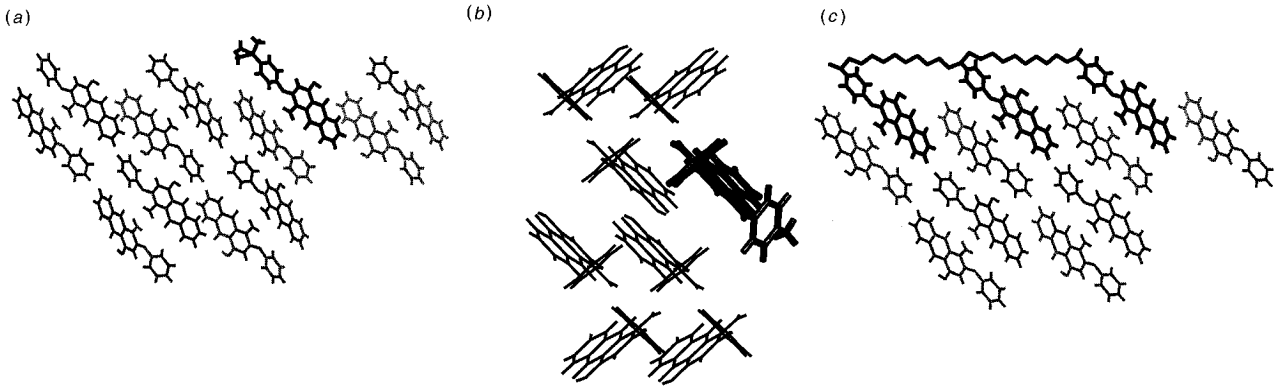



**Fig. 3** Possible binding sites of additives: (*a*) **2** on (101), (*b*) **3** on (020), and (*c*) **4** on (101)

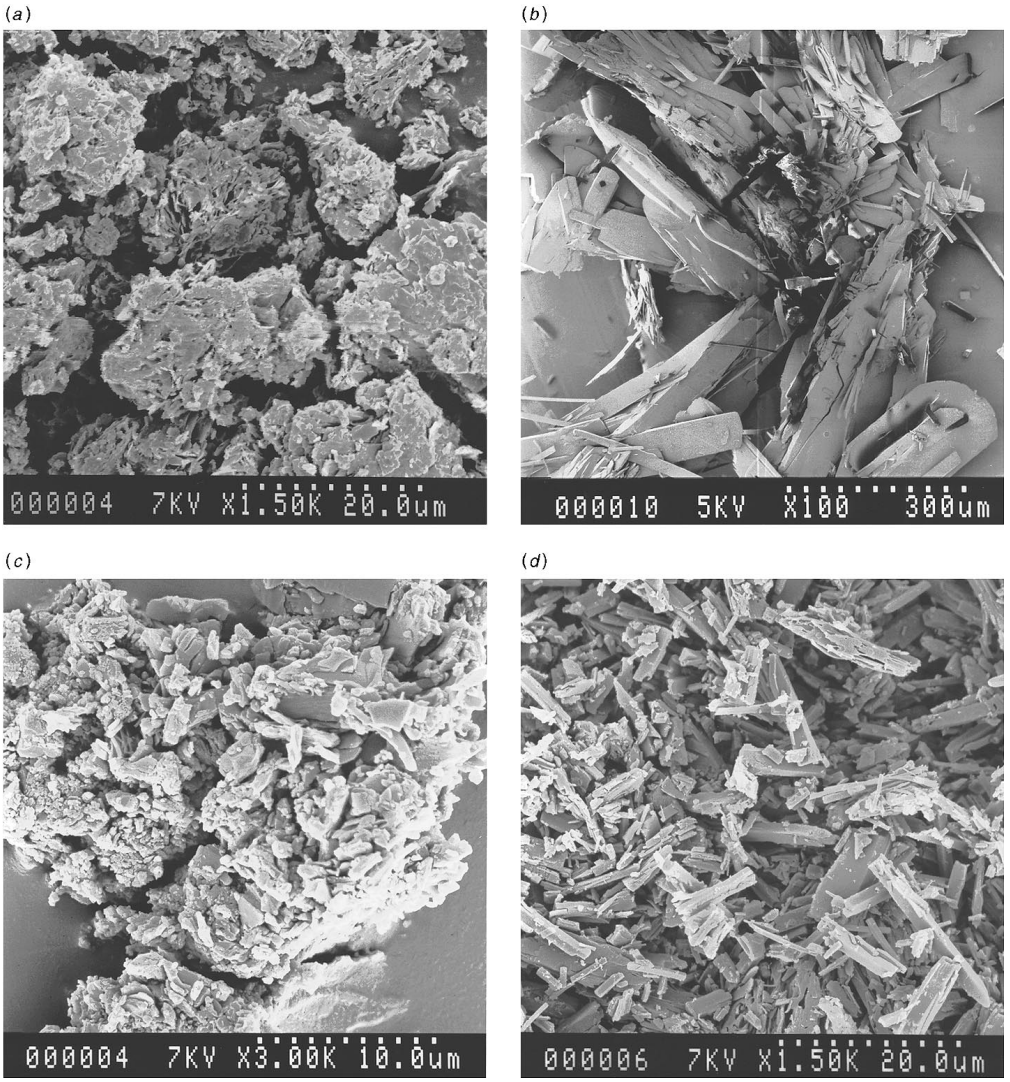



**Fig. 4** Crystals grown from solution in the presence of (*a*) **2**, (*b*) **3**, (*c*) a mixture of **2** and **3** and (*d*) polymer **4c**

## Results

### Characterisation of polymers

Three copolymers were prepared, having mole fractions (as determined by FTIR) of 0.048, 0.11, and 0.16 vinylphenol. This suggests a reactivity ratio of vinylphenol with styrene of unity, in agreement with related studies.[13] After grafting, 2.25, 4.7 and 12.8% (w/w) of 1-amino-2-bromo-4-hydroxyanthraquinone had been incorporated, and the copolymers had weight mean molar masses ($M_w$) of 168100, 103300 and 85700, respectively. They are referred to subsequently as polymers **4a**, **b** and **c**.

### Solution grown crystals

Fig. 4(*a*)–(*d*) shows crystals grown in the presence of the *tert*-butyl derivative **2**, the 4-methylaniline derivative **3**, a mixture of **2** and **3**, and polymer **4c**, respectively. When compared with crystals grown from pure solutions [Fig. 2(*a*)] it is quite clear that all the additives tested had a significant effect on the crystallisation process. The *tert*-butyl derivative appeared to prevent the formation of well defined crystals, yielding a powder of irregular plate-like crystals. The toluidino derivative significantly reduced growth along the *b*-axis as expected, while polymer **4c** appeared to give enhanced nucleation (smaller crystals) but little morphological change. Overall these results indicated that the additives chosen were of sufficient potency to test in polymer films.

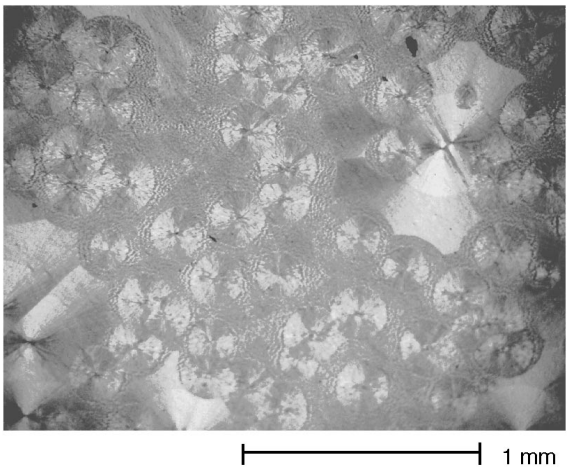



**Fig. 5** Spherulitic crystallisation of **1** in a polymer film

### Crystallisation in polymer films

In polymer films dye nucleation was followed by radial growth, giving polycrystalline spherulitic or rosette type morphologies which eventually spread through the entire film. This is seen in Fig. 5. Similar behaviour has been reported previously for anthraquinone crystallising from polystyrene films.[14] Powder X-ray diffraction of crystallised films had major reflections corresponding to *d*-spacings of 1.23, 1.15, 0.62 and 0.49 nm as expected for *b*-axis needles of this dye having predominant {101} and {002} faces.[13] This implies radial growth of the spherulites along the fast growing [010] direction. Increasing the dye concentration from 0.28 to 0.85 wt.% led, as expected, to an increase in the nuclei density from 0.7 to 3.5 rosettes per mm$^2$ due to the associated rise in supersaturation.

In agreement with the solution growth experiments reported above, all the additives influenced the crystallisation of the dye in the polymer film. The morphological changes are shown in Fig. 6. Fig. 6(*a*) and (*b*) show the effect of increasing levels of **2** while Fig. 6(*c*) and (*d*) show the effects of **3** and polymer **4c**, respectively. Clearly, all these additives inhibit the formation of the space-filling rosettes and appear to inhibit the crystallisation process such that large areas of the film remain uncrystallised.

In order to quantify the magnitude of crystallisation inhibition, simple kinetic studies were undertaken in which the rosette numbers and radii were measured. The resulting crystallisation times and nucleation densities are shown in Fig. 7(*a*) and (*b*), where it is clear that stabilisation of the dye films is enhanced by increasing concentrations of additive. Compound **3** is most active in this respect, presumably because it was designed to inhibit the fastest growth direction, [010]. The polymers appear to be particularly successful at inhibiting nucleation, an observation that appears to be in complete contrast to their solution behaviour, where they appear to enhance the nucleation rate. This may well be related to reduced mobility and conformational flexibility in the polymer film. Finally, the behaviour of the three grafted copolymers was compared and the kinetic data are shown in Fig. 7(*c*). For comparison, polystyrene was also tested and found to be ineffective in modifying the crystallisation and also to be immiscible with the silicone binder system used here. Given that these copolymers contain significant polystyrene blocks it would be expected that their solubility in the polymer film would be a key factor in their efficacy. For example, polymer **4a** is 95.5% polystyrene, which implies a low solubility in the film and hence explains its poor efficacy in Fig. 7(*c*). Polymers **4b** and **4c** showed improved performance, although at high (10%) levels they also phase separate in the film. It is perhaps surprising that the efficacy does not increase monotonically with level of grafting, yet it is encouraging that all the polymers

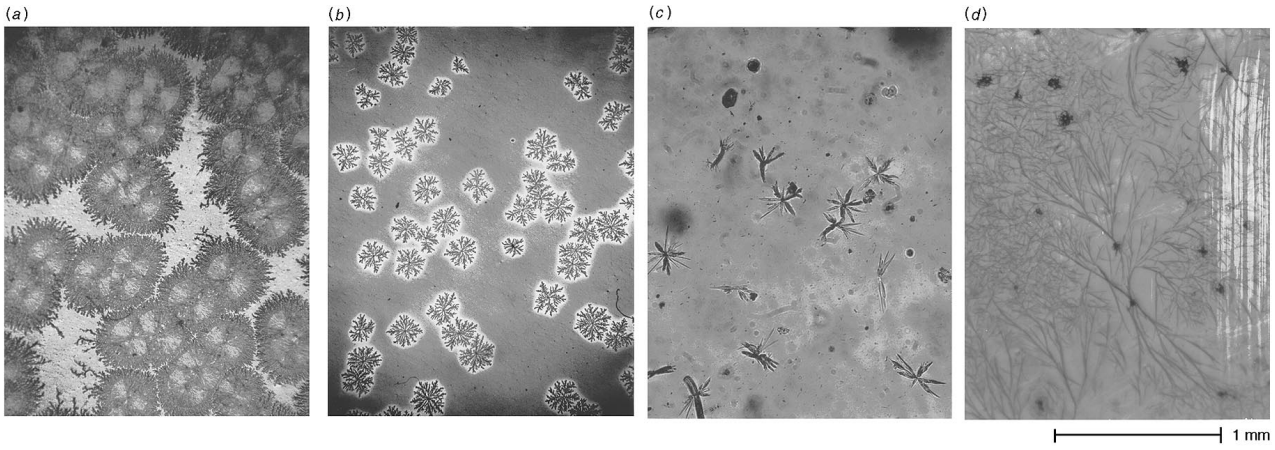



**Fig. 6** The influence of additives on the morphology of crystallised polymer films: (*a*) 5% of **2**, (*b*) 14% of **2**, (*c*) 2% of **3** and (*d*) 5% of **4c**

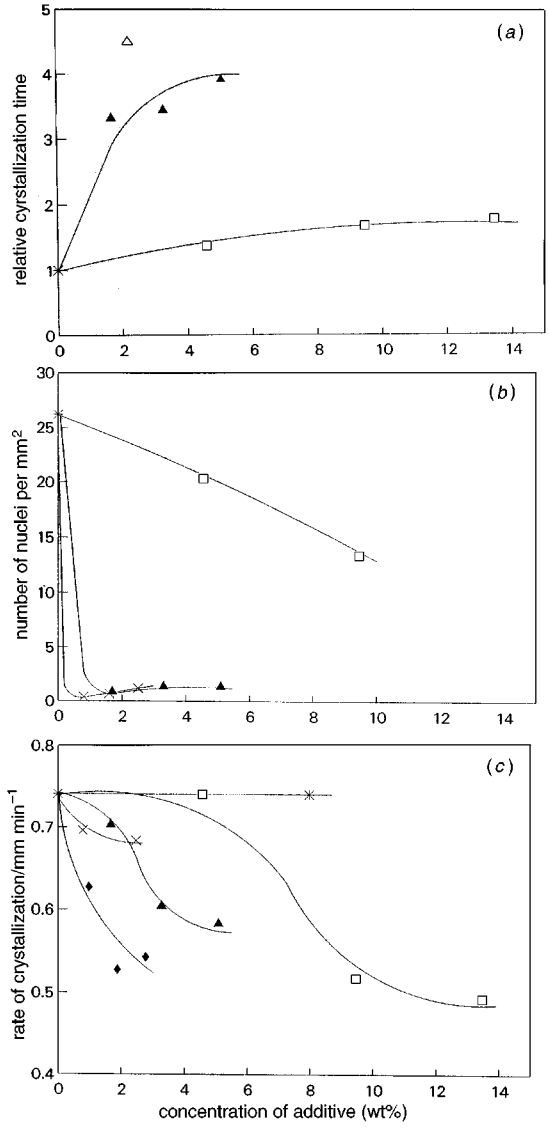



**Fig. 7** The influence of additives on the kinetics of crystallisation of **1** in polymer films: (*a*) the effect of (□) **2**, (△) **3**, and (▲) polymer **4c** on times taken for films to fully crystallise, (*b*) the effect of (□) **2** and polymers (×) **4a** and (▲) **4c** on the nucleation in films, and (*c*) the effect of (*) polystyrene, (□) **2** and polymers (×) **4a**, (◆) **4b** and (▲) **4c** on crystallisation rates

show enhanced activity over the single small molecule *tert*-butyl derivative. This supports the idea that efficacy may be enhanced through multidentate binding.

## Conclusions

This study has applied the structurally based strategy for selection and design of tailor-made growth auxiliaries to the case of an anthraquinone dye crystallising from an amorphous polymer film. Crystallisation inhibitors, selected on the basis of the known crystal structure of the dye, were tested for efficacy in solution growth experiments and shown to be powerful crystallisation modifiers. It is interesting to note that unlike previous studies of tailor-made inhibitors the molecular recognition features involved utilise only van der Waals and $\pi$–$\pi$ interactions rather than more specific hydrogen bonding. It was found that this behaviour could be transferred directly to crystallisation in a polymer matrix, with the result that crystallisation could be significantly inhibited and the dye films stabilised even at temperatures as high as 100 °C. This correspondence between solution and polymeric media has not been addressed before, although it is clearly of significance both technologically and from the biomineralisation viewpoint.

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