

Modelling of paint-film curing by fractals

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We have studied surface heterogeneity that arises during curing of paint films formed with alkyd-melamine formaldehyde systems. Surface heterogeneity is quantified by fractal dimension. Heterogeneous surfaces exhibit higher fractal dimension than uniform surfaces. Mathematical modelling of the surface reaction is carried out by Monte Carlo simulation technique. *n*-Butylated melamine formaldehyde crosslinker produces less heterogeneous films than isobutylated one and is explained based on solvent evaporation and reaction rates. Introduction of viscosity changes during solvent evaporation in the model, decreases the extent of reaction, more so for isobutyl melamine formaldehyde system. In butyl, besides higher overall conversion, more uniform films result, primarily due to higher uniform solvent evaporation.

Fractals describe disordered systems and disorder can be described in terms of nonintegral dimension, known as fractal dimension^{1,2}. A disordered system inherits substantial physical and chemical properties of the ordered system, as long as the deviations from the ordered state are small. If the disorder is strong little could be learnt from the ordered systems.

The fractal concept addresses such strongly disordered systems. It treats disorder as an intrinsic rather than a perturbation phenomenon. A system is weakly disordered if the disorder vanishes at progressively smaller length scales (continuum models) or at progressively larger length scales (lattice models). In strongly disordered systems, disorder persists at smaller as well as larger scales (scale-invariant) and there exists no reference state for comparison.

Fractals involve chance, i.e. both their regularities and their irregularities are statistical, and there is increasing evidence that it is found in abundance in nature. The random patterns of clouds and coastlines are fractals. Examples of some of the fractal processes in science and engineering are diffusion-limited aggregation, fluid flow in porous media, motion of air bubbles in oil, metal electrodeposition and electrical discharges^{3,4}. Fractal theory has been successfully used to describe substantially different phenomena like growth of a rough surface, formation of particle gels and colloids, the fingering of a viscous fluid, and formation of linear and branched polymer matrices.

The fractal dimension of a physical object is a scale-

invariant property, and it is independent of many details of how the object is formed. A simple model that neglects most of the complexity of a real system should, nonetheless, describe the properties of the system correctly. The fractal dimension unlike the ordinary dimension is expressed as a fraction. While a straight line is one-dimensional, a random-coiled polymer chain in solution has a dimension between 1 and 2. The more nearly a flat fractal object fills a plane, the closer its dimension approaches 2. A square or a triangle is two-dimensional, but the surface of a solid catalyst usually has a dimension between 2 and 3.

The concept of a fractal surface has been used to a limited extent in systems of interest to chemists and chemical engineers. Computer simulations have been performed on metal electrodeposition⁵, three-dimensional particle aggregation⁶, etc. In these studies the fractal surface has been successfully used to describe particle properties such as roughness and shape and the effects these have on mass and momentum transfer. Very little application is found in the area of surface coatings; our focus in this paper is on characterizing fractal nature of curing reactions in paint films. In general, curing reactions are complex, nonuniform and heterogeneous and the heterogeneity involved is not clearly understood. It should be borne in mind that, although iterated fractals that are self-similar can be constructed, self-similarity is true of real fractals found in nature only in a statistical sense, that is natural objects are random, and a piece will not look exactly like the whole. Also, a natural fractal is not self-similar over all lengths of scale. There are both upper and lower size limits beyond which a natural object is no longer fractal. Stanley & Meakin⁷ and Borman⁸ have reviewed fractal phenomena in physics and chemistry.

Nonuniform curing of films leads to nonvisible and visible defects. While visible defects like cratering, blushing, sagging, etc. have been well characterized and understood⁹, nonvisible defects which arise due to nonuniform curing¹⁰ have not been studied thoroughly. The theory of fractals is a good tool to characterize these types of surface heterogeneity and helps in quantifying them.

We have studied the crosslinking reaction between a crosslinker and an alkyd and subsequent curing to form a film using Monte Carlo simulation techniques. Monte Carlo techniques study chemical systems by looking at

the random character inherent in many chemical and physical processes, and they usually present a simpler mathematical approach than is accomplished with more conventional theories. The technique is based on the principle that any complex process can be broken down into a series of simpler independent events (i.e. a Markov chain), each represented by a probability distribution. Future events are determined by the present state and are independent of the past. The approach is computationally intensive, but the computer code is significantly simpler than that needed for other numerical approaches. Monte Carlo simulation technique has been used for describing adsorption/desorption processes, molecular diffusion, sampling procedures, annealing processes, in analytical chemistry, etc.^{11,12}

Experimental

The alkyd is prepared by reacting phthalic anhydride, glycerol and coconut oil¹³. Two different crosslinkers, viz. isobutylated and *n*-butylated melamine formaldehyde, were used in the study. The difference in performance between the two crosslinkers is explained based on solvent evaporation rates. Bauer and coworkers^{14,15} studied crosslinking chemistry and network formation of MF-acrylate systems. Mukesh *et al*¹⁶ studied the MF-alkyd system.

The alkyd resin used had a weight average molecular weight of 5000 with respect to polystyrene GPC standards, with a hydroxyl excess of 17%. No pigment was used in the formulation. It was made from coconut oil/phthalic anhydride/glycerol combination by standard recipe¹³. Two melamine formaldehyde-based crosslinking agents were used. The first one was partially isobutylated and the other partially butylated with molecular weights of 2900 and 3000 respectively. The functional groups of melamines¹⁷ were characterized by interpreting the ¹H NMR spectra.

Films were prepared by applying a mixture of alkyd and crosslinker on thin glass slides using a bar coater. Film thicknesses were approximately 300–350 Lm. The films were cured in an air-circulating oven for different periods of time. Usually, films were made in duplicate or in triplicate.

Some of the cured films were dipped in methyl isobutyl ketone (MIBK) for 1 h with the glass plate. The glass panels were then taken out and dried to remove MIBK at 120°C in an air-circulating oven for 30 min. The film obtained after MIBK treatment and drying usually had spots which appeared as craters (see section below). These spots were seen prior to removal of excess MIBK as well. Further details of the experimental procedure and characterization were described elsewhere¹⁶.

Results

Figures 1, *a* & *b* are scanning electron micrographs of films prepared with isobutylated and *n*-butylated melamine formaldehyde resins and cured at 120°C for 30 min. The former film was (figure 1, *a*) rough and discordant with uneven surface, while the latter (figure 1, *b*) was smooth and uniform. Figures 2, *a* & *b* show the films formed with isobutylated and *n*-butylated systems respectively, cured at 125°C for 30 min, and later treated with MIBK. The films exhibit surface deterioration or erosion due to solvent penetration into the film followed by evaporation.

At 125°C the film formed with *n*-butylated MF and alkyd appeared to be smooth and uniform when compared to isobutylated system, indicating higher conversion (hence higher insolubles) and more cross-linking. This may be due to higher boiling point of *n*-butanol (lower and uniform solvent evaporation rate),

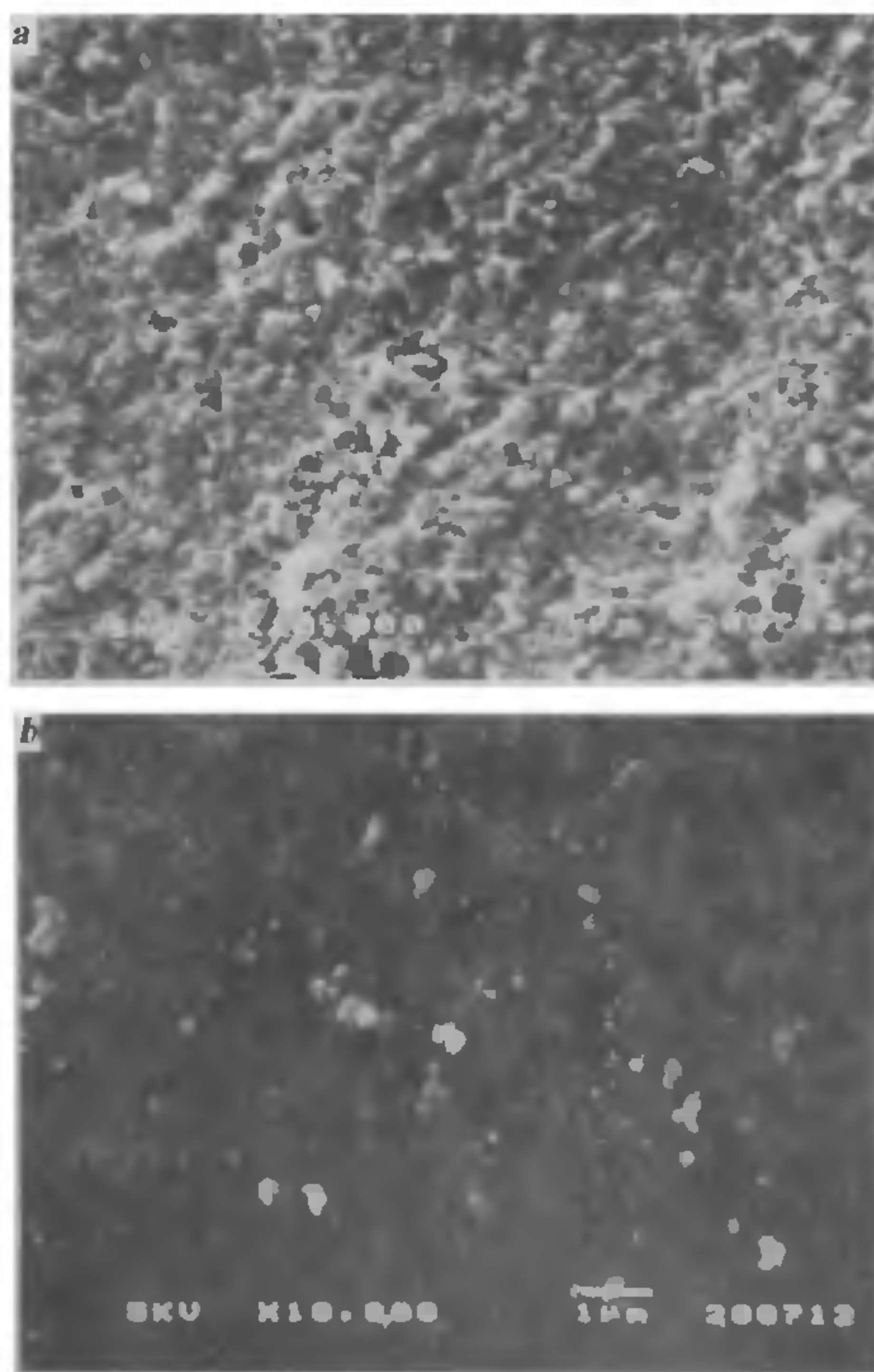


Figure 1. Scanning electron micrograph of cured films (120°C, 30 min) with (a) isobutylated and (b) *n* butylated melamine formaldehyde and crosslinker.

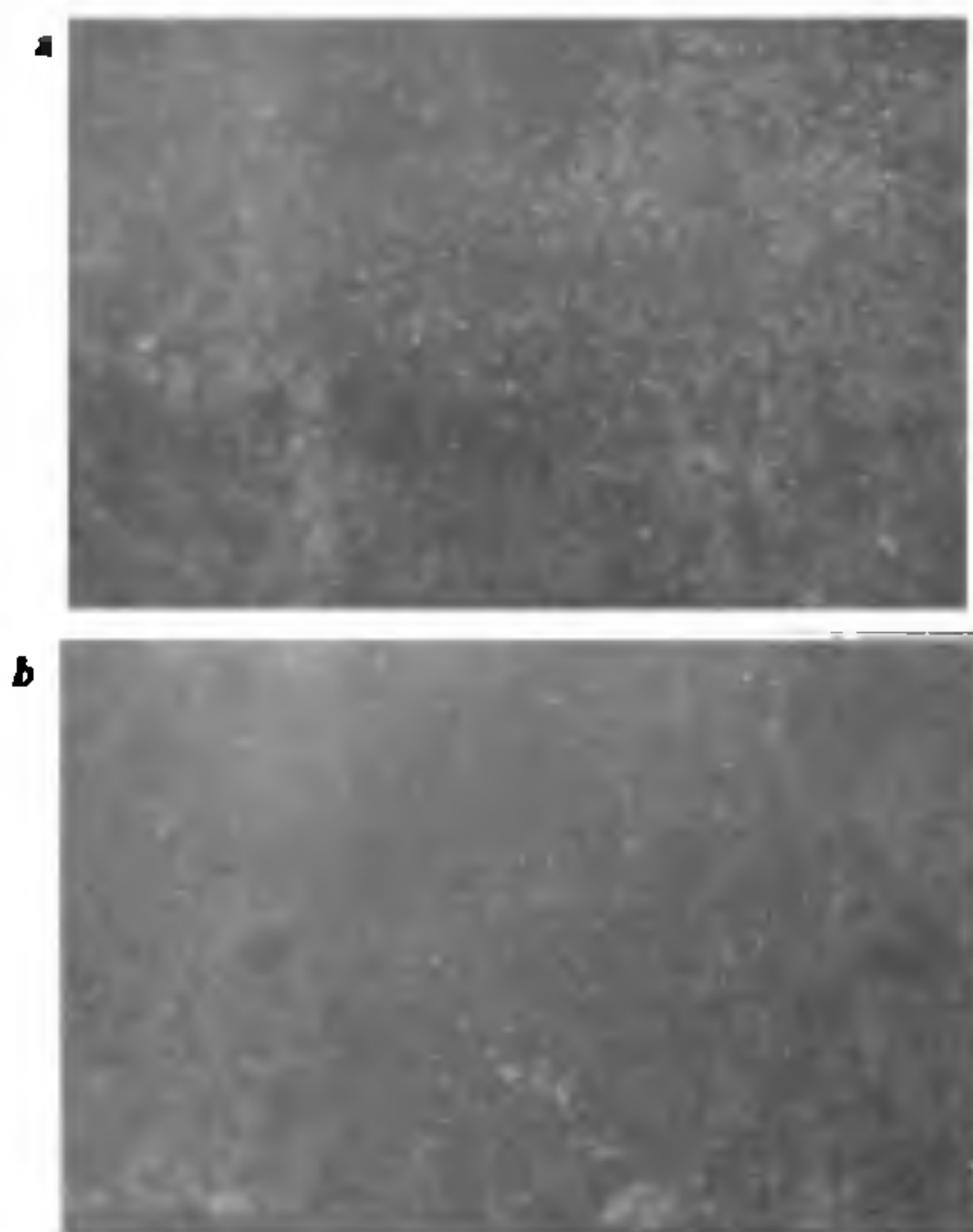


Figure 2. Photographs of cured films dipped in methyl isobutyl ketone and dried later in oven (a) isobutylated and (b) *n*-butylated melamine formaldehyde.

which leads to higher conversion and crosslinking. The MIBK-treated films appear rough and heterogeneous (fractal). Although the surface erosion observed with MIBK films is an indication of the extent of crosslinking, it is not an accurate measure of the conversion. Bauer and Dickie¹⁸ looked for evidence of blushing, puckering and softening of MF-acrylate films treated with a few drops of the solvent methyl ethyl ketone, and concluded that the solvent resistance increases with cure temperature and melamine concentration.

Mathematical model

The crosslinking reaction consists of the following:



where *A* and *B* represent melamine formaldehyde and polyol respectively. *S* is the solvent, and in the present case either *n*-butanol or isobutanol. Equation (1) represents solvent evaporation which is a function of solvent vapour pressure, curing temperature, exposed area for evaporation, solvent diffusion and solvent-to-polymer interaction in the solution mixture. The second

step is the actual reaction step to form the product *P*, and during reaction one mole of solvent is also liberated.

The differential equations describing the generation and consumption of various species with time are given as

$$d[S]/dt = -k_e[S] + R_r, \quad (3)$$

$$d[A]/dt = d[B]/dt = -d[P]/dt = -R_r, \quad (4)$$

where *R_r*, the rate corresponding to reaction, is given as

$$R_r = k_r[A][B]/C_T. \quad (5)$$

Initially at *t*=0, *C_T*=[*A*]₀+ [*B*]₀+ [*S*]₀ and at any time *t*, *C_T*=[*A*]+ [*B*]+ [*P*]+ [*S*]. The reaction rate is assumed to be dependent on the concentrations of [*A*] and [*B*].

The reaction takes place on a surface where the paint is applied, thereby producing a heterogeneous two-dimensional film. The variation of product formation on a two-dimensional rectangular surface is modelled by the Monte Carlo simulation technique¹⁰. In the simulation the rectangular area is divided into *N* × *N* equal cells, which are independent of one another, where reaction steps (1) and (2) are assumed to take place. The simulation procedure is given in Appendix 1.

Figures 3, *a* & *b* depict the surface after 400 time steps for two different sets of rate constants. The concentration of the product in each cell is represented by a number between 0 and 9, where 0 indicates no product formation (i.e. complete absence of reaction) and 9 indicates total conversion. Figure 3, *a* describes the surface for high-evaporation-rate constant *k_e*. The surface is highly heterogeneous with regions of total conversion (9) and no conversion (0). Such films do not possess uniform property and are therefore not desirable.

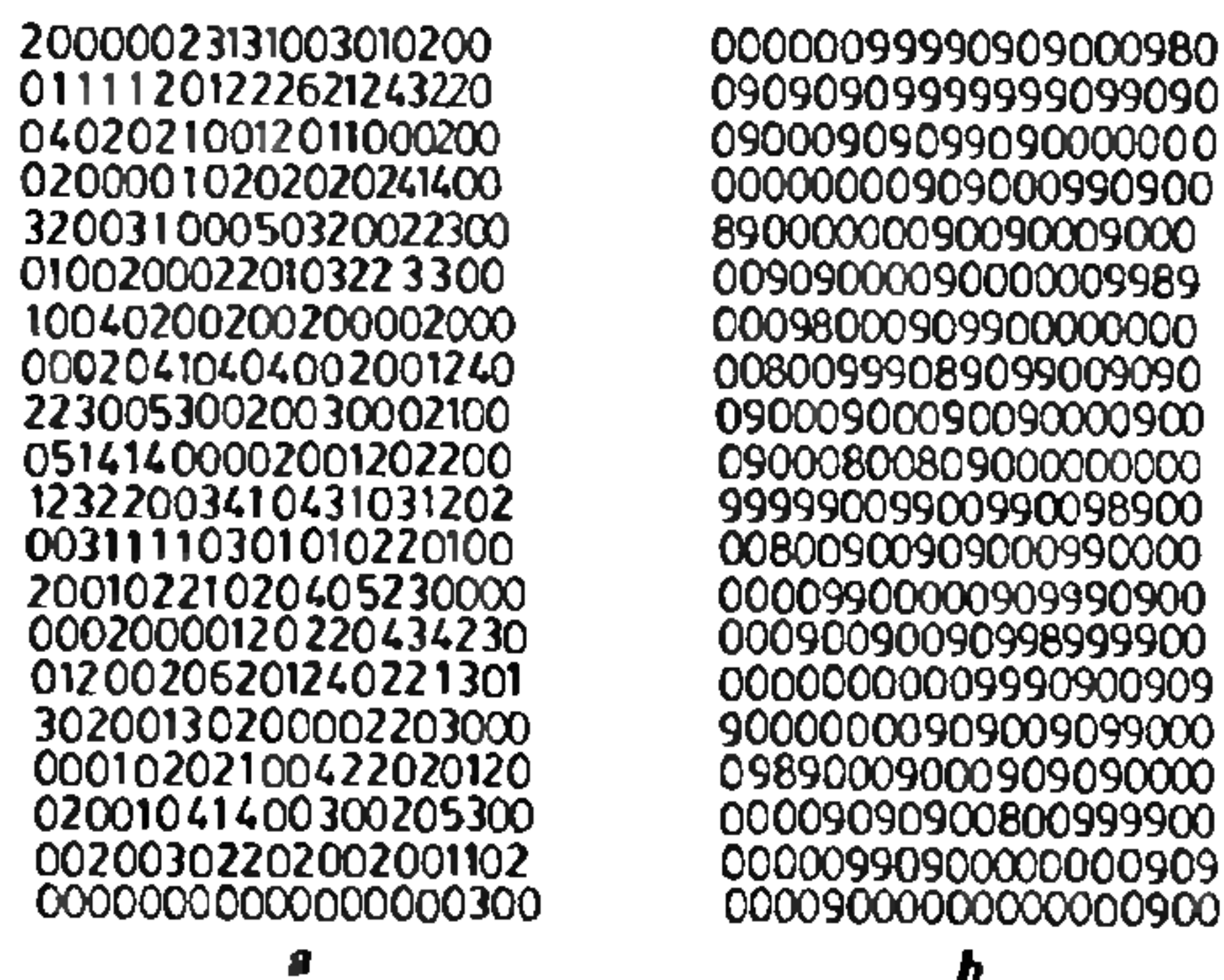


Figure 3. Monte Carlo simulation of a surface for (a) High-solvent-evaporation rate (*k_e*=0.9) and (b) low-solvent-evaporation rate (*k_e*=0.2).

When the evaporation rate is low a more uniform film is formed (Figure 3, b). Here the conversion and product formation are fairly constant over the entire matrix region. It is seen from the simulations that k_e has significant effect on film formation.

Fractal dimension

The surface due to irregular conversion at different points is heterogeneous. One measure of surface heterogeneity is determining the product surface density as a function of annular region. If the conversion is uniform throughout the simulation region, the surface density at each annulus has to be the same. A difference in the surface density will be an indication of surface heterogeneity. The surface is divided into nine annular regions and the surface density (which equals the amount of product in the region/area of the annular region) is estimated in each region. In general terms, the surface density (ρ) and the radius of the annular region (r) are related as

$$\rho \propto r^n, \quad (6)$$

where for a homogeneous surface the exponent n should be equal to zero, i.e. density is independent of r . A non-zero value for n is an indication of surface heterogeneity and larger the value, larger is the nonuniformity of the film. Exponent n should be related to the fractal dimension, d_f and the Euclidean dimension d as

$$n = d - 1 - d_f \quad (7)$$

Since the film formation is studied by modelling on a surface the Euclidean dimension in this case will be equal to 2. When the surface is uniform and n approaches zero the fractal dimension will be equal to 1. Equations of the form shown above are used in systems where the surfaces are created in a random manner, viz. electrodeposition¹⁹, fractal growth⁴, deposition on fibres and surfaces⁶, etc. The fractal dimension in all these cases are in the range of 1.1 to 1.7.

A plot of $\log \rho$ against $\log r$ is shown in Figure 4 for three different cases. The figure indicates that the relationship between ρ and r (given by equation (6)) holds well. The fractal dimension can be estimated from slopes as described in equation (7). The slope generally is negative, indicating a lower surface density at outer annular regions than the inner ones. Decrease in density with increasing radius has been observed in many fractal growth processes⁴.

Figure 5, a plots the change in fractal dimension of curing with time for two simulations, viz. one with high-solvent evaporation and reaction rates and the other with low rates. The fractal dimension shoots up to almost 2 and decreases with time and reaches the

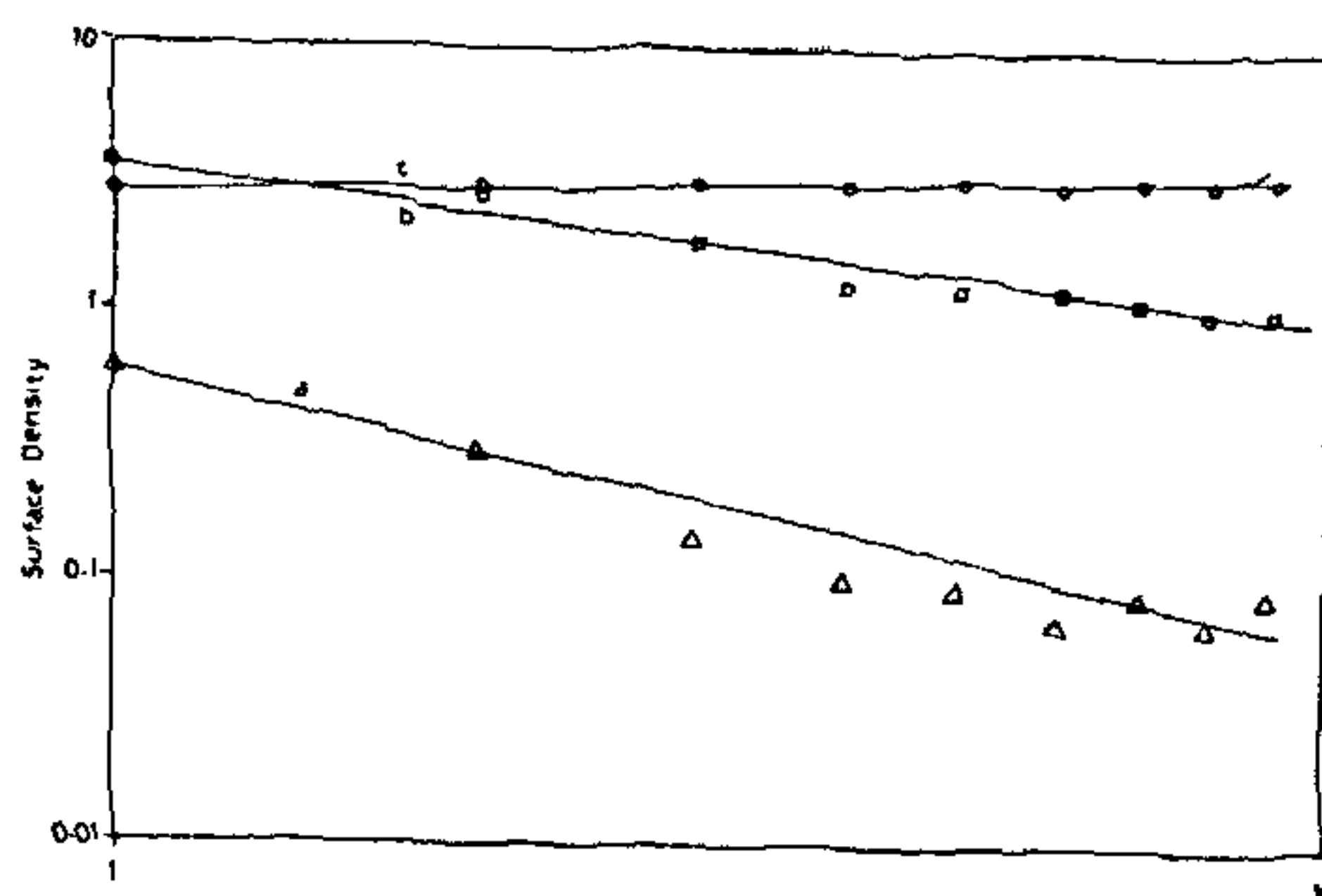


Figure 4. Double-log plot of surface density versus annular radius r . a. $k_r = 5$, $k_e = 10$, time = 25; b. $k_r = 0.2$, $k_e = 0.2$, time = 200; c. $k_r = 0.2$, $k_e = 0.2$, time = 2000.

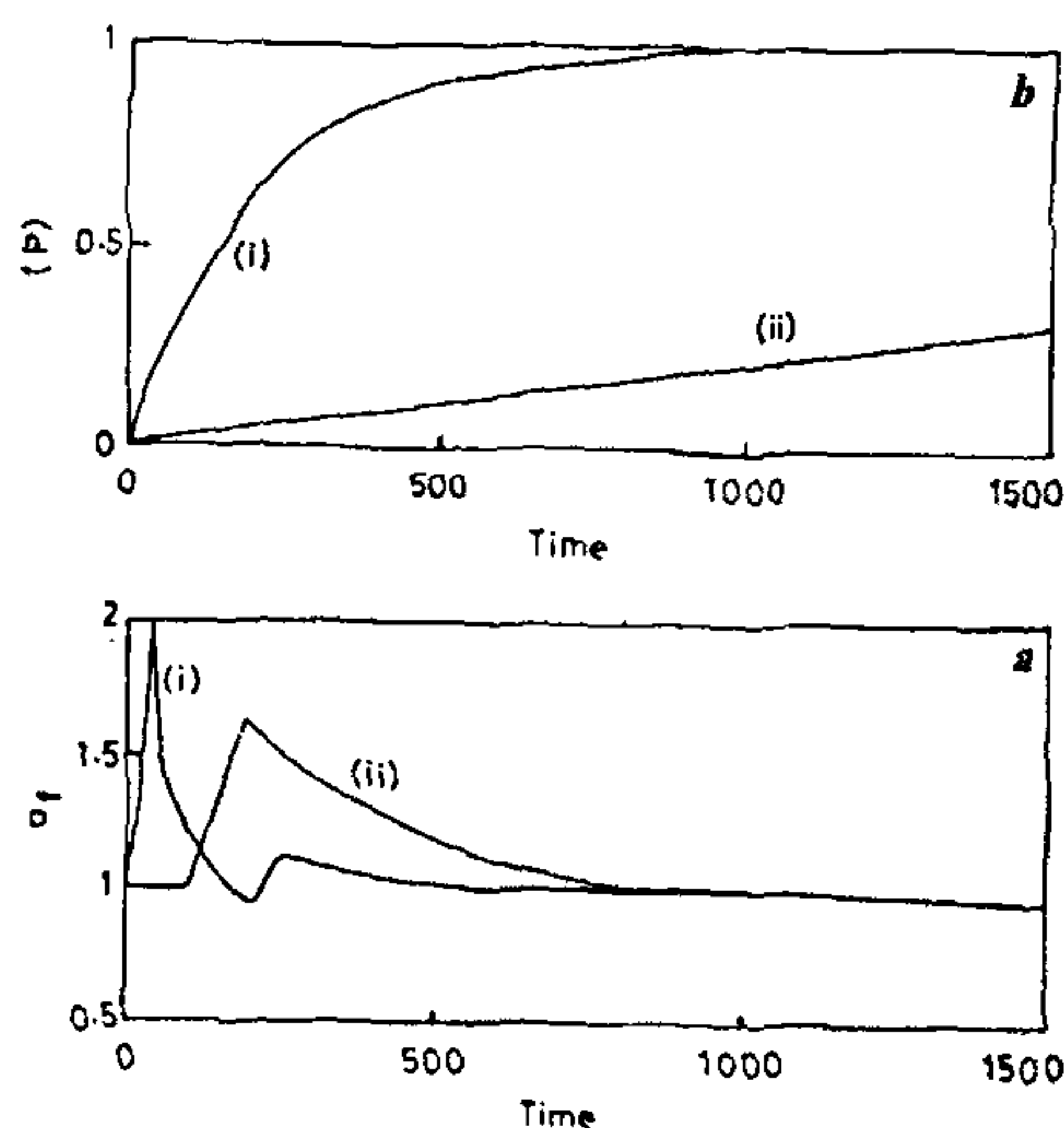


Figure 5. Simulation time as a function of (a) fractal dimension and (b) product amount. Reaction rate constant independent of viscosity. (i) $k_r = 5$, $k_e = 10$; (ii) $k_r = 0.2$, $k_e = 0.2$.

final value of 1 with an undershoot of 0.85. A fractal dimension less than 1 indicates that the surface density of the outer annular regions is greater than the inner ones, while a value greater than 1 indicates a reverse situation. A fractal dimension of 1 indicates an uniform surface. When solvent evaporation and reaction rate constants are small, the rate of product formed is low. The fractal dimension, in this case, slowly rises to 1.6, and drops gradually over a longer period of time. Initially, the high-solvent evaporation case (curve (i), Figure 5) exhibits higher fractal dimension than the low-

solvent evaporation case (curve (ii), Figure 5), but after a short period of time, the former exhibits lower fractal dimension than the latter.

In the modelling studies mentioned so far it is assumed that the viscosity of the solution remains unaltered. In reality, viscosity rises with solvent evaporation leading to decrease in molecular diffusion and hence the rate of reaction. Diffusion coefficient is generally considered directly proportional to the square root of viscosity²⁰, in which case the reaction rate constant will be a function of solvent amount as

$$k_r \propto \sqrt{[S]} \quad (8)$$

Incorporation of equation (8) with (3) to (5) leads to simulation as shown in Figures 6, a & b. In this case, reaction rates and conversions are low when solvent evaporation is low, and when the solvent evaporation rates are very high. At very high-solvent-evaporation rate (Figure 6, b, Curve (iv), due to increase in solution viscosity, the reaction rate decreases with decrease in solvent amount as given by equation (8). Generally for all rate-constant values the fractal dimension estimated now is less (< 1.7) than the values obtained for the viscosity-independent case, indicating that less heterogeneity is observed when reaction-rate constant is assumed to be a function of solvent amount than when it is considered independent of it. Comparison of the simulation of low-solvent evaporation (curve (ii), Figure 6) and high-solvent evaporation (curve (iv), Figure 6) cases for the same reaction-rate constant show that conversion is higher in the former than the latter case, while the fractal dimension exhibits a reverse trend: is

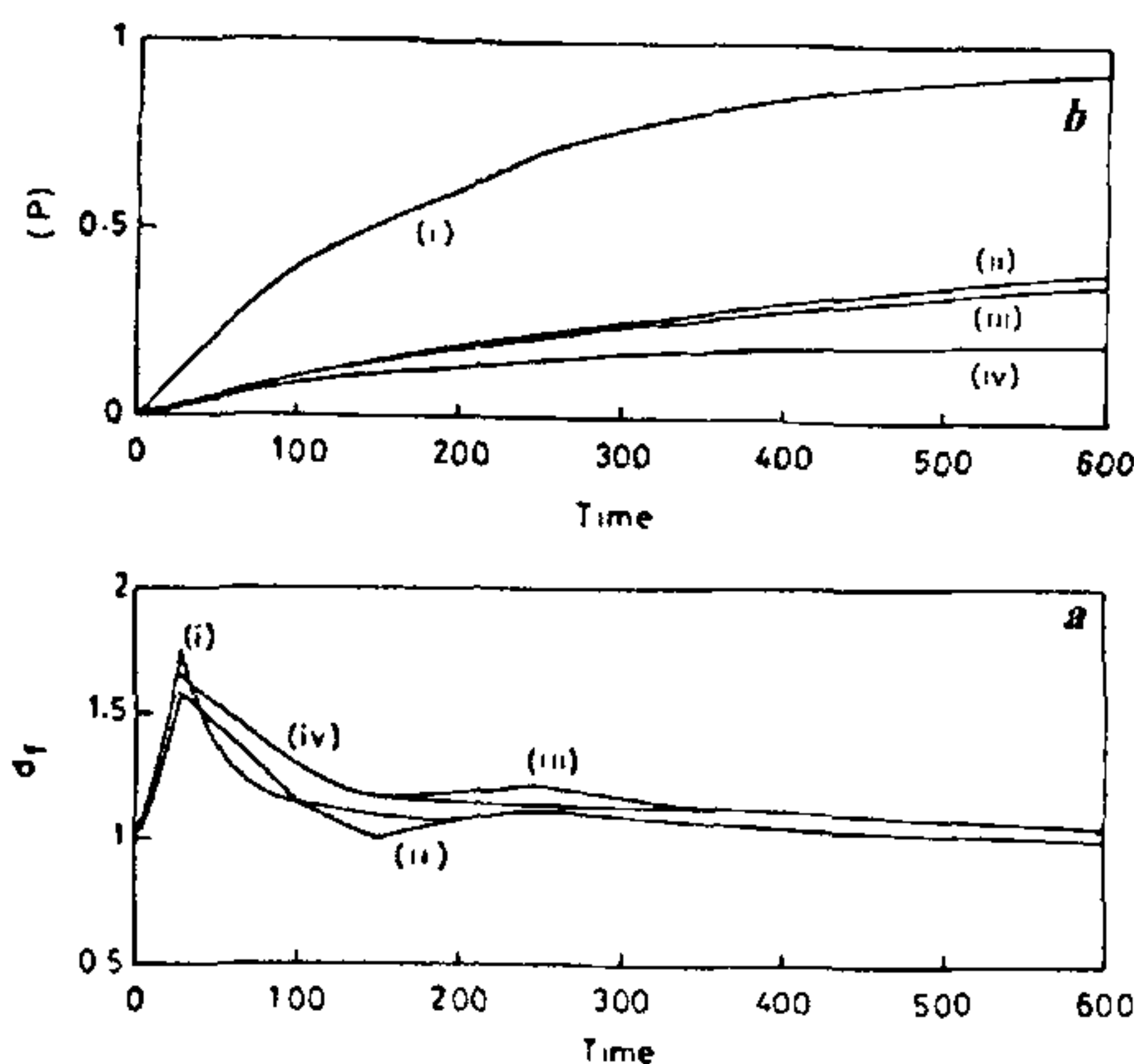


Figure 6. Simulation time as a function of (a) fractal dimension and (b) product amount. Reaction rate constant is a function of viscosity $k_r \propto [S]^{\frac{1}{2}}$. (i) $k_r = 4$, $k_e = 15$; (ii) $k_r = 0.5$, $k_e = 0.15$; (iii) $k_r = 0.5$, $k_e = 1$; (iv) $k_r = 0.5$, $k_e = 15$.

higher in the latter than the former case. This indicates that higher conversion does not necessarily lead to higher surface heterogeneity, but on the contrary to a more uniform film. *n*-Butanol with a higher boiling point than isobutanol (by about 10°C) has a lower solvent-evaporation rate than isobutanol, leading to higher conversion and crosslinking (as seen from experiments), but, at the same time, producing more uniform and less heterogeneous film than films prepared with isobutanol.

Conclusion

This article demonstrates the use of theory of fractals in understanding the curing reaction between melamine formaldehyde and alkyd. Film heterogeneity is quantified by fractal dimension. The polymerization reaction on a surface is modelled by Monte Carlo simulation and the fractal dimension determined from the surface density. Fractal dimension increases initially with time indicating uneven conversion on the surface in early stages, later decreases and reaches a value of 1. Fractal dimension in some of the random growth processes like aggregation, electrodeposition, deposition on fibres, etc. are found to be in the range of 1.1 to 1.7.

Incorporation of viscosity effects in the model alters the formation of heterogeneous films. Increase in solution viscosity due to solvent evaporation leads to decreased molecular mobility and hence decreased conversion. The model predicts that high solvent-evaporation rate case will lead to low conversion and more heterogeneous films than low solvent-evaporation rate case. Fractal dimension appears to be a powerful technique for quantifying and comparing heterogeneity, which is observed in a wide range of chemical and physical process.

Appendix I

The Monte Carlo simulation procedure consists of the following steps for 20×20 cells.

1. Generate a random number i between 1 and 20 and a random number j between 1 and 20. The reaction is assumed to take place in cell X_{ij} .
 2. For given k_e and k_r recalculate the concentration of $[A]$, $[B]$, $[P]$ and $[S]$ from equations (3)–(5) in cell X_{ij} . (At $t=0$ the concentration of all the species is known.)
 3. At each time step repeat steps (1) and (2).
- For a given set of rate constants the accumulation of the product P , with time over the 400 cells is simulated by the procedure outlined above.

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Unusual growth of smectic A liquid crystals

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Smectic A liquid crystals have been found to grow from the isotropic phase in the very unusual form of long cylindrical structures in some binary mixtures of smectogenic and non-mesomorphic aliphatic compounds. We report some experiments which show that the occurrence and stability of these structures can be accounted for by a concentration gradient of the non-mesomorphic component. In such a case it is necessary to include a linear term in curvature in the elastic energy density of the system.

SMECTIC A liquid crystals are characterized by a layered arrangement of long organic molecules which are approximately parallel to one another (Figure 1)¹⁻³. The structure within the layers is that of a fluid, so that the medium is a 1D crystal (along the z-axis say) and a 2D liquid. In a perfect monodomain sample (Figure 1) the layers are flat and separated from their neighbours by a fixed spacing d , which is usually of the order of the molecular length. The elastic constant for compression along the layer normal is very large ($\sim 10^8$ erg cm⁻²). On the other hand, the fluid layers can bend easily, preserving the layer spacing. The corresponding curvature elastic constant K is rather small ($\sim 10^{-6}$ dyne). Usually samples prepared between two glass plates have such bent layers, giving rise to point or line defects, about which the molecular orientation changes abruptly. The geometrical constraints require that the line defects form sets of confocal ellipses and hyperbolae⁴.

When the smectic A phase separates from either the nematic phase which has only a long range orientational

order, or the isotropic phase, it usually does so in the form of bâtonnets⁴ (Figure 2) which are somewhat elongated objects. This growth pattern has been studied in great detail by Fournier and Durand⁵ recently. The smectic A liquid crystal can be expected to have an anisotropic interfacial tension γ , and the formation of bâtonnets is a consequence of $\gamma_{\parallel} > \gamma_{\perp}$, where the subscripts \parallel and \perp refer to directions in relation to the layer-normal. The bâtonnets are structures in which the low value of K is exploited to minimize the area of the surface parallel to the layers exposed at the interface (Figure 3).

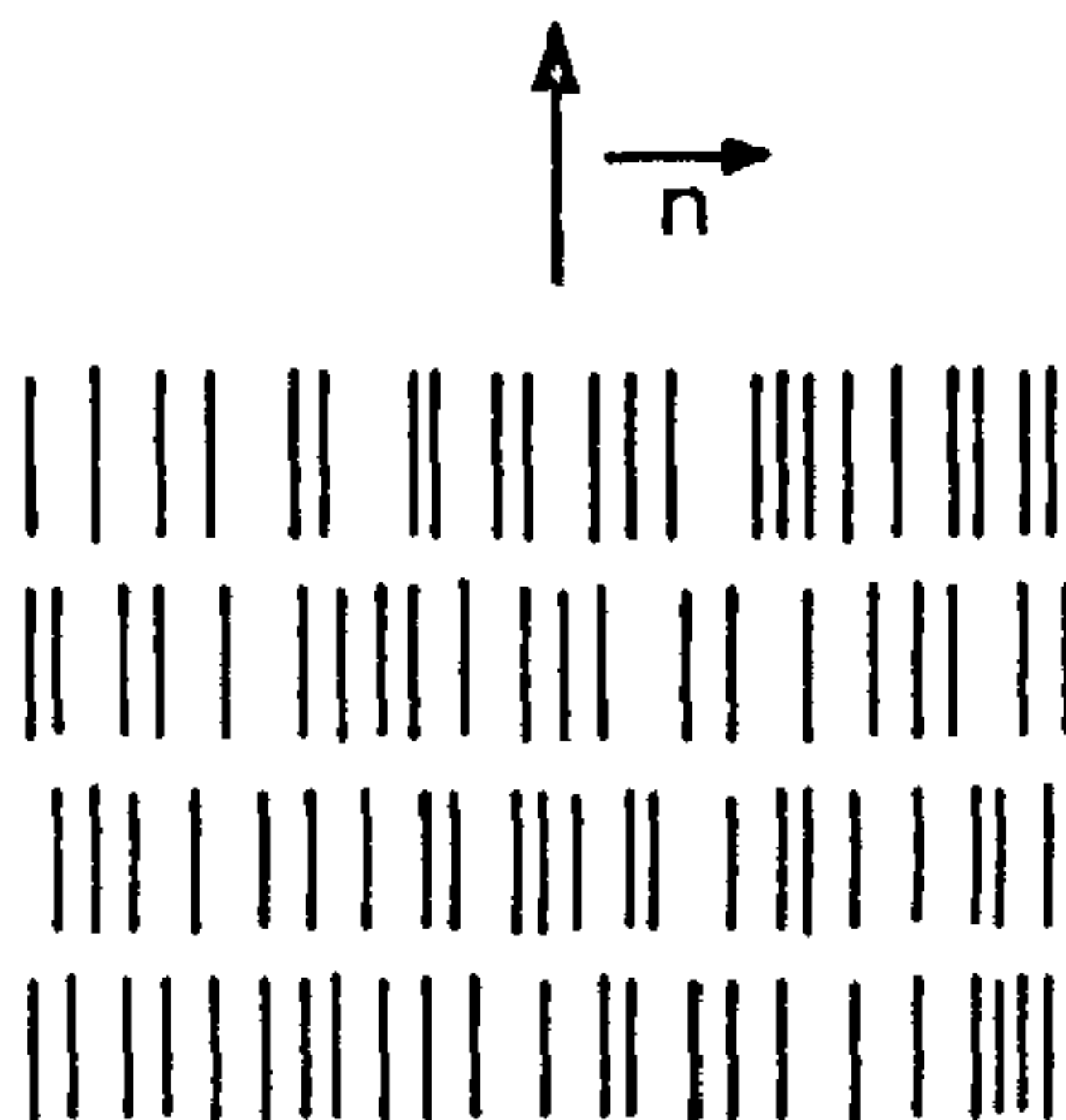


Figure 1. Schematic representation of the molecular organization in a smectic A liquid crystal