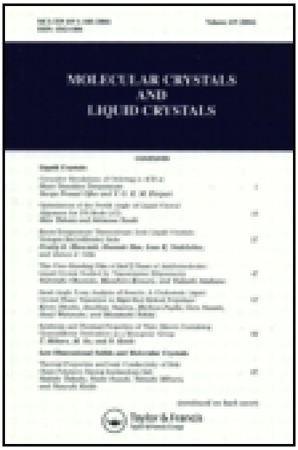

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Dissolution Kinetics in Langmuir-Blodgett Films of Solid State Polymerized ω-Tricosenoic Acid

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DISSOLUTION KINETICS IN LANGMUIR-BLODGETT FILMS OF SOLID STATE POLYMERIZED ω-TRICOSENOIC ACID

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Abstract ω-tricosenoic acid in L.B. films undergoes a solid state, lattice controlled polymerization. This molecule exhibits high contrast under short time development when used as an electron-resist in microlithography. This high contrast seems to be due to two factors : the monodispersity of the polymer and the compactness of the film. To check for a relationship between these factors and contrast, a model for the dissolution rate of partially polymerized L.B. films is presented, which includes monodispersity and compactness as basic hypotheses.
Since this model is able to fit all the set of experimental results in spite of its crude simplicity and the small number of adjustable parameters, it is believed to actually represent the real dissolution mechanism. The necessity of introducing a long penetration period is an expected consequence of the compact, trans-zigzag structure of the fatty acids. Polymer monodispersity is a second consequence of the model. A possible mechanism for it (stress limited propagation) is presented.

INTRODUCTION

ω-tricosenoic acid in L.B. layers undergoes a solid state, lattice controlled, polymerization[1-2]. When used as an electron resist, this molecule exhibits a contrast which is high and which increases when the development time is reduced[3-4]. These properties, which are unique for an in situ polymerized resist (negative resist), are suspected to be due to two simultaneous factors :

i) the compact layered structure of the L.B. film, giving rise to a special dissolution kinetics.

ii) polymer monodispersity, arising possibly from the stress limited character of the propagation.

Since no direct access to these two properties is possible, they can only be checked through their consequences. The aim of this paper is to check them in a field where they are key parameters, namely dissolution kinetics.

RESULTS

A microscopic model for the dissolution of partially polymerized L.B. films has already been presented elsewhere[4]. Figure 1 shows the results derived from this model for several development times. These results apply to 30 layers of a molecule undergoing first order polymerization. On the same figure are also plotted the experimental results obtained with 29 layers of ω-tricosenoic acid. The model contains only two parameters. These two parameters are adjusted from the fit of the "5s" curve and no more degree of freedom is left to fit the curves corresponding to other development times. In spite of the small number of parameters and the lack of freedom for adjustments, the model is able to fit the whole set of experimental results. Therefore, it is believed to describe the actual mechanism of dissolution.

By changing hypotheses and laws in the model and looking at the effect on the results, it is possible to point out the key features of the mechanism and to examine their consequences, which lead to arguments in favour of compactness and monodispersity. It turns out that only two hypotheses are important :

i) development has to consist of two <u>successive</u> steps : penetration and extraction. The existence of a long penetration period (80 % of the monomer development time) is indicative of high compactness ;

ii) the penetration speed of the solvent has to be highly homogeneous. This is an argument for the low dispersity ot the polymer.

On the other hand, the penetration and extraction laws are of very little importance, provided homogeneity is preserved.

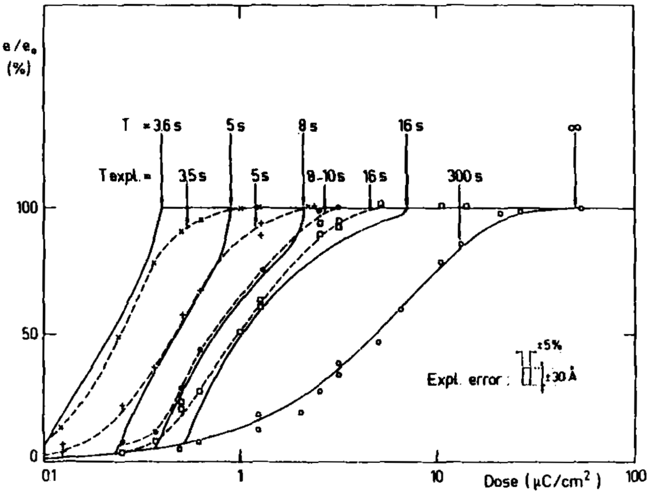

FIGURE 1. Dissolution kinetics for a monomer-polymer mixture in L.B. layers. Abscissa : dose sent onto the film (5 keV electrons). Ordinate : relative thickness of the film remaining after development. Full lines represent the results computed for 30 layers from the model of ref. 4. Dotted lines are experimental results for 29 layers of ω-tricosenoic acid. T is the development duration for curve computation. T_{expl} is the experimental development duration.

DISCUSSION

Compactness of the film

The increase both in contrast and sensitivity upon development shortening (fig. 1) arises from the rapid increase of the penetration period with polymer concentration (going from 0 to 10% polymer doubles the penetration time). This mechanism is efficient only if the penetration period is a non-negligible fraction of the development time. In this respect, Langmuir-Blodgett resists behave very differently from classical resists. None of the previous dissolution models applying to classical spin-coated resists[5-6-7] had to introduce an induction period to fit experimental results. In Langmuir-Blodgett layers, on the other hand, most of the development time is spent in penetration. This is due to the close-packed, compact structure of the aliphatic chains which has already been described many times in the literature.

Dispersity of the polymer

The results about speed homogeneity derived from the model show that, if the penetration speed is not microscopically homogeneous, two main consequences arise :

i) Even for a small speed scattering, the end of the penetration time (i.e. the time when the solvent reaches the substrate and when extraction starts) is slightly spread in time and this smoothens the join between the sloping part of the exposure curve and the 100 % plateau. This effect is very sensitive to polymer dispersity, especially at short development times. This is indeed observed, but only to a small extent.

ii) For larger speed scattering, penetration and dissolution speeds are spread in time and in dose and this should predictably give rise to a contrast decrease, especially large at short development times when speed scattering is crucial. Not only is not this effect observed, but the opposite, i.e. a contrast increase, is observed.

These two results are consistent with a very low dispersity of the polymer. The reason for this low dispersity is not well understood. A possible mechanism for it might be a stress-limited propagation : if the slight unavoidable mismatch between the monomer lattice parameter and the polymer period adds up at every step of the propagation, it may reach the 4 Å reactivity limit[8], then stopping the polymer length every time after the same number of links (Fig. 2).

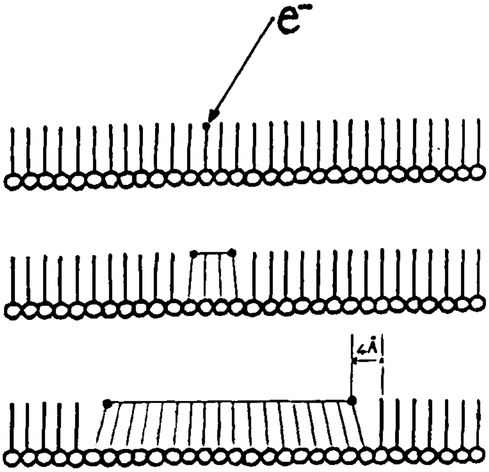

FIGURE 2. Stress-limited propagation.
top : initiation.
middle : propagation.
bottom : stress above reactivity limit stops propagation.

This feedback mechanism automatically yields a monodispersed polymer. This mechanism, which is unlikely in crystals made of small molecules, is not unreasonable in monolayers of long chain fatty acids. It can be understood in the following way. In a Langmuir-Blodgett monolayer, the polar heads are rigidly attached to one another. Furthermore most of the hydrophobic chain is held in position by Van der Waals interactions, which are strong in these solids. Hence the lattice forces are believed to be much stronger than in crystals made of small molecules, and may be large enough to impose their structure in spite of the stress induced by the propagation.

Since there is no direct evidence for this stress-limited propagation, we tried to substitute another mechanism for stress in propagation stopping. A few percents of C_{17} ω-double-bonded acid was introduced into the C_{23} ω-double-bonded one by forgetting a purification step in the course of the synthesis. This shorter molecule acted as an impurity and reduced the propagation length (i.e. the sensitivity) by a factor of 10. Since this impurity was randomly distributed the result was a drastic decrease of the contrast, which could not be kept above 0.7.

This is an argument in favour of a stress-limited propagation, but the problem is still open.

CONCLUSION

This dissolution model which is able to fit experimental results well in spite of its crudeness and its lack of freedom seems to actually correspond to the real mechanism of dissolution. As such, it has been used to check which are the polymer properties which strongly influence the dissolution kinetics in Langmuir-Blodgett films : film compactness is one, polymer dispersity is the other. The compactness and the dispersity of ω-tricosenoic acid have been checked through the dissolution kinetics of partially polymerized films of this molecule. The film is found to be highly compact, and the polymer seems mono- or very little dispersed. Compactness in Langmuir-Blodgett films is a well-known phenomenon. Monodispersity on the other hand is not well understood. It might be due to a propagation self limitation due to the stress induced by the propagation itself.

REFERENCES

1. A. Barraud, C. Rosilio, A. Ruaudel-Teixier, Jour. Colloid Interface Sci, 62, 509 (1977).
2. A. Barraud, C. Rosilio, A. Ruaudel-Teixier, Thin Solid Films, 68, 91 (1980).
3. A. Barraud, C. Rosilio, A. Ruaudel-Teixier, Thin Solid Films, 68, 99 (1980).
4. A. Barraud, Thin Solid Films, 85, 77 (1981).
5. S, Fujimori, Jour. Appl. Phys., 50, 615 (1979).
6. J.S. Greeneich, J. Electrochem. Soc. (SSST), 122, 970, (1975).
7. F.H. Dill, A.R. Neureuther, J.A. Tuttle, E.J. Walker, IEEE Trans Electron Devices, 22, 456 (1975).
8. G.M.J. Schmidt, in Reactivity of Photoexcited Organic Molecules, Wiley (New York), p.227 (1967).