

Furfuryl alcohol conjugated oligomer pellicle formation

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Abstract

The heterogeneous acid catalysis of furfurylic alcohol oligomer polymerisation was investigated for the first time. Oligomer conjugated bond structures were confirmed through their optical absorption bands at 570, 650, 770 and 930 nm. Polymerisation in the furfurylic alcohol surface inside glass tubes produced porous pellicles that fell as a result of gravity, breaking apart when tube radii were larger than 0.27 cm. The high oligomer concentration at the furfurylic alcohol surface caused the formation of oligomer clusters that bound to each other to generate the porous and electrically conductive pellicle. Oligomers produced by heterogeneous catalysis have a molecular weight distribution richer in small oligomers than those produced by homogeneous catalysis. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Conjugate oligomers; Furfurylic alcohol; Heterogeneous catalysis

1. Introduction

Furfuryl alcohol, FA, polymerisation by homogeneous acid catalysis has been studied extensively [1–3]. The end product of this polymerisation reaction is a black nonconducting resin [3]. The admixture of the monomer and a concentrated acid catalyst, such as HCl, produces a highly exothermic reaction that is completed shortly after the addition of acid. In catalyses by weak acid solutions, the first stages of polymerisation are characterised by oligomers that impart bluish to brown colours to the FA solution, according to the degree of reaction [3–5]. The optical absorption bands of these solutions are attributed to bond conjugation of the oligomer chain, as was proposed by Gandini et al. [1,3,5]. Above 10 monomers, instead of the conjugated bonds, polymer growth is characterised by the branched structure of the insulating resin [3,6]. The reason for this behaviour is still not understood.

Furfuryl alcohol is a bifunctional compound; positions 5 and hydroxyl group, shown in Fig. 1, are the most reactive. Under acid catalysis first stages of polymerisation goes through a condensation reaction between these two positions. Several aspects of this condensation reaction are still not very clear [1]. Conjugated oligomers with odd number of monomers are understood, Fig. 2. However, when there is an even number of monomers, conjugation

cannot be established along the whole chain without further instability of the product.

This paper presents and discusses a novel heterogeneous catalysis process for FA polymerisation. Oligomers are formed in the FA liquid surface exposed to the vapours of a highly concentrated HCl solution. The unusual mechanical properties of the reaction products are discussed and correlated with the measured optical absorption bands and electrical conductivity.

2. Experimental

Surface FA polymerisation was carried out in borosilicate glass U tubes whose internal radius ranged from 0.02 cm to 0.27 cm. The glass tubes were filled with fresh vacuum distilled furfuryl alcohol and immediately exposed to the vapour of a HCl 12 N solution. A blue layer was generated and began to fall shortly after insertion of the glass U tube into the acid chamber, as shown in Fig. 3. The dependence on time of the layer position was measured using a scale, a convergent lens (10 cm focal length) as a magnifier and a chronometer. Experiments were also conducted with FA/DCM solutions to define the dependence of the falling speed on liquid density. A few experiments were also conducted with a FA-acetone solution. Because the acetone solutions were less dense, the speeds observed were higher. Experiments with higher acetone concentrations produced a discontinuous, intermittent flow of bluish oligomer packets. In these cases, longer times were necessary for the pellicle

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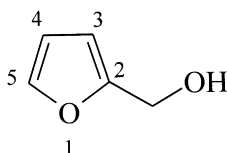


Fig. 1. 2 Furfuryl alcohol molecule.

to be built, but once formed, their speed was the highest observed in this study. Preparation of the oligomer for optical measurements was done in a more convenient set-up, as shown in Fig. 4. The reaction products were taken from the spherical reservoir after 5.0 min reaction.

Optical absorption measurements in the UV–visible and near infrared spectra were taken using a Cary 17-A spectrophotometer using two quartz cells with 10 and 0 mm optical length. In order to adjust optical absorption peaks to a maximum 3.0 OD, the original solutions were diluted with FA or DCM.

Electrical conduction measurements of the pellicle generated in the FA surface were made, as follows. Two droplets of pure FA were spread on a clear glass plate having two vacuum evaporated gold electrodes. The width of the glass plate and the distance between the gold electrodes were 2.5 and 1.5 cm, respectively. During the experiments an ohmmeter was permanently connected to the gold electrodes. The FA liquid film completely filled the space between the electrodes. The liquid surface was exposed to acid vapour from a concentrated P.A. HCl acid glass bottle. Immediately after exposure, the spread FA became green, after which it gradually turned black. Electric resistance was continuously measured during this procedure.

3. Results and discussion

3.1. Mechanical properties

The products of the polymerisation reaction in the AF–HCl vapour interface fell continuously and, after a few minutes, produced a blue liquid column in the upper part of the glass tube. The interface between the transparent pure FA liquid and the bluish zone was always found to be sharp as seen with the help of the simple magnifier. The shape of the interface is approximately round, as shown in Fig. 5, and does not change during motion. Curvature radii increased as the glass tube radius decreased. When the HCl vapour was removed from the AF exposed surface, the oligomers already produced maintained the same speed of fall. Figs. 6 and 7 show, respectively, the displacement with time and the corresponding speed of the bluish layer for several glass

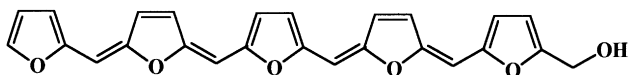


Fig. 2. 5 monomer conjugated oligomer from furfuryl alcohol.

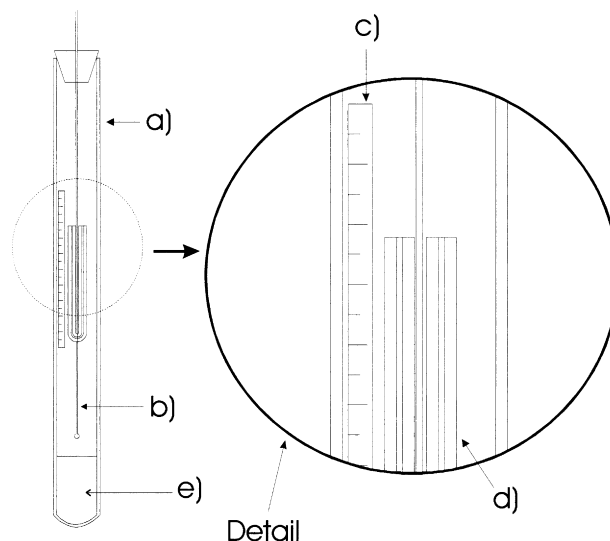


Fig. 3. Apparatus for measuring the speed of fall of an oligomer pellicle: (a) acid vapour chamber; (b) thermometer; (c) scale; (d) glass U tube; and (e) hydrochloric 12 N acid solution.

tube radii. Similar experiments were performed with FA/DCM solutions, as shown in Fig. 9. In the case of glass tubes with a radius over 0.27 cm, the blue layer breaks apart shortly after being generated. For even larger diameters, pea-like droplets of black polymer are produced.

The results of the above described experiments can be summarised as follows. The speed of fall, V , of the blue layer in a given glass tube is constant (Fig. 8). The speed for different glass tube radii, R , is dependent on the square of each tube's radius and, for a given tube radius, on the square of the difference in density, between the oligomer

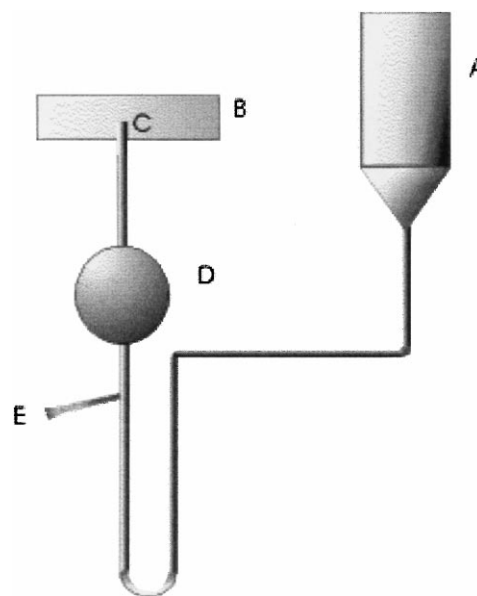


Fig. 4. Set-up for oligomer production: (a) furfuryl alcohol; (b) HCl solution vapour chamber; (c) glass tube filled with furfuryl alcohol; (d) oligomer reservoir; and (e) drain for the oligomer solution.

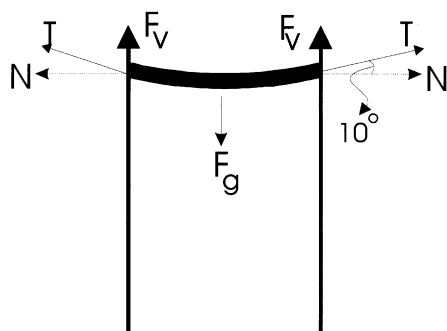


Fig. 5. Forces acting on the pellicle. F_g , pellicle weight minus buoyancy; N , attracting force between pellicle and glass tube wall; F_v , friction force around the pellicle rim; T , mechanical tension on the pellicle.

and the liquid, $\Delta\rho$, as shown in Fig. 8. Therefore, $V = f(R^2, \Delta\rho^2)$.

Fresh FA constantly reaches the surface, thus continuously causing the polymerisation reaction. This behaviour indicates that the blue layer is a porous pellicle, as will be confirmed later on. For a glass tube radius over 0.27 cm, the pellicle's mechanical strength is surpassed by the mechanical tension generated by its own weight, buoyancy and the forces of interaction with the tube wall.

To investigate the nature of the falling substance, further experiments were made on the bubbling vapour of an HCl solution, carried out by a pure N_2 gas stream, in freshly distilled FA inside a beaker. The same bluish colour developed, but oligomer separation from the solution did not occur even by centrifugation. Vigorous shaking of the glass tube while the pellicle was falling resulted in stopping its motion. These experimental findings are a clear indication that oligomers are arranged in large aggregates bound to each other to form the pellicle.

The falling motion of pellicles can be understood as deriving from the following forces: the action of gravity, weight and buoyancy, F_g , and a viscous force, F_v , around the

rim of the pellicle, as illustrated in Fig. 4. The following holds true for constant speeds:

$$F_g = F_v \tag{1}$$

F_g and F_v being given by

$$F_g = \pi R^2 \delta \Delta\rho g \tag{2}$$

$$F_v = 2\pi R \delta \beta V^n \tag{3}$$

Therefore,

$$V^n = \frac{Rg\Delta\rho}{2\beta} \tag{4}$$

where δ is the pellicle thickness, β and n are constants to be determined from experimental data, $\Delta\rho$ is the difference in density between the liquid and oligomers, R is the glass tube radius, while the remaining symbols have their usual meaning. Taking into account the experimental result

$$\left(\frac{V}{R^2}\right) = (1.4 \text{ cm}^{-1} \text{ s}^{-1}) \quad \text{for} \quad \Delta\rho = 0.115 \text{ g/cm}^3 \tag{5}$$

and Eq. (4), it turns out that

$$n = 1/2 \quad \text{and} \quad \left(\frac{g\Delta\rho}{2\beta}\right)^2 = 1.4 \text{ cm}^{-1} \text{ s}^{-1} \tag{6}$$

The above equation gives the right dependence, found experimentally, between the fall speed and $\Delta\rho$, shown in Fig. 9, and 1.250 g/cm^3 for the oligomer density.

Pellicle rupture for a glass radius over 0.27 cm can be understood considering the mechanical stress, T , necessary to keep the pellicle's shape. The mechanical stress components are F_v and N , as shown in Fig. 5. N originates from oligomer–glass attraction interaction. T calculated for the 0.27 cm radius glass tube gives a good estimate of the pellicle's mechanical strength. This was done taking into account that $\Delta\rho = 0.115 \text{ g/cm}^3$ for the pellicle fall in its

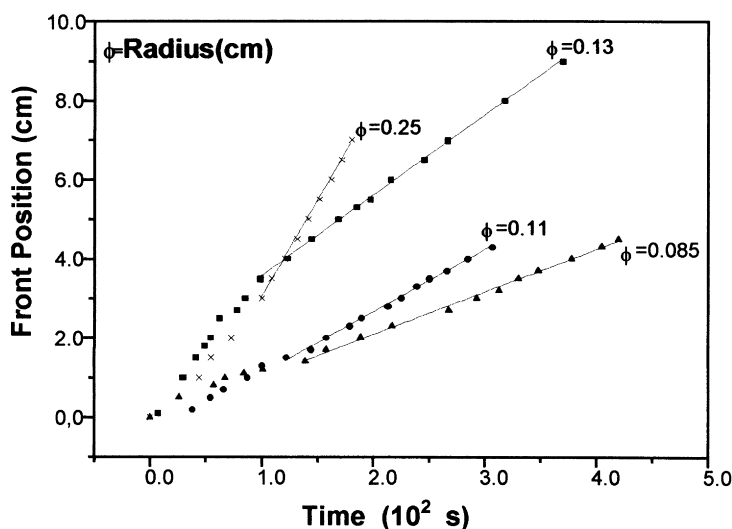


Fig. 6. Pellicle displacement with time in glass tubes with radius ranging from 0.25 to 0.085 cm.

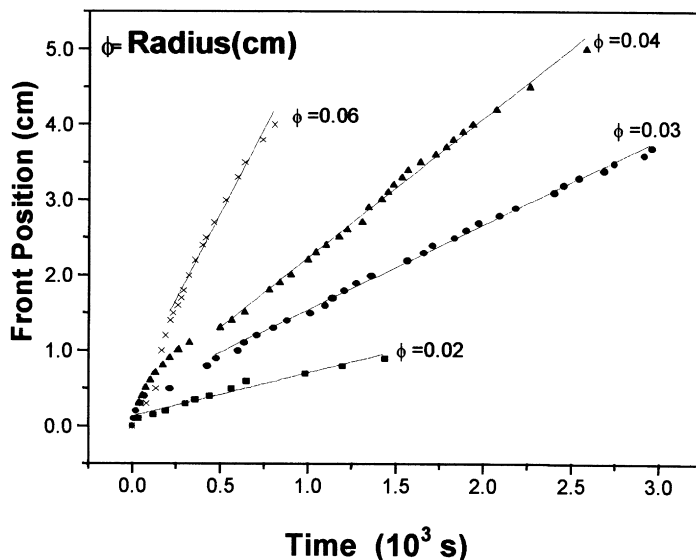


Fig. 7. Pellicle displacement with time in glass tubes with radius ranging from 0.06 to 0.02 cm.

monomer. The angle, shown in Fig. 4, was found to be $\alpha = 10^\circ$ for the 0.27 cm glass tube. The pellicle's tensile strength found was 8.0 Pa, which is 6 orders of magnitude lower than the tensile strength of polyethylene. This result, together with the need for pellicle porosity to explain the continuous polymerisation reaction at the surface, points to a structure consisting of oligomer aggregates bound to each other.

The above results can be understood as follows. Heterogeneous catalysis by a high acid concentration at the FA liquid surface produces a high oligomer concentration. As soon as a critical oligomer concentration is reached, large aggregates are formed and grow. Aggregates are arranged to form a porous pellicle. The pellicle's fall moves oligomers off the surface, arresting the fast polymerisation reaction. It was further observed that, in glass tubes with smaller diameters, the fall speed is so low that oligomers stay longer

in the surface layers, where polymerisation reaction kinetics is high and, instead, produces black insulating resin.

3.2. Optical absorption spectra

The optical absorption spectra of the following solutions where studied: (a) produced by bubbling HCl vapour in FA; (b) in the 0.085 cm radius glass tube; (c) produced in a 0.11 cm radius glass tube; (d) oligomer solution from the 0.085 cm capillary neutralised by triethylamine. The spectra are shown in Figs. 10–12 and 13, respectively. All optical spectra have a normalised 360 nm peak. The OD of the oligomer optical absorption band, while in the pellicle, was not measured. Sample preparation for optical measurements destroyed the oligomer aggregates, resulting in uniform and stable solutions. If there was any particular

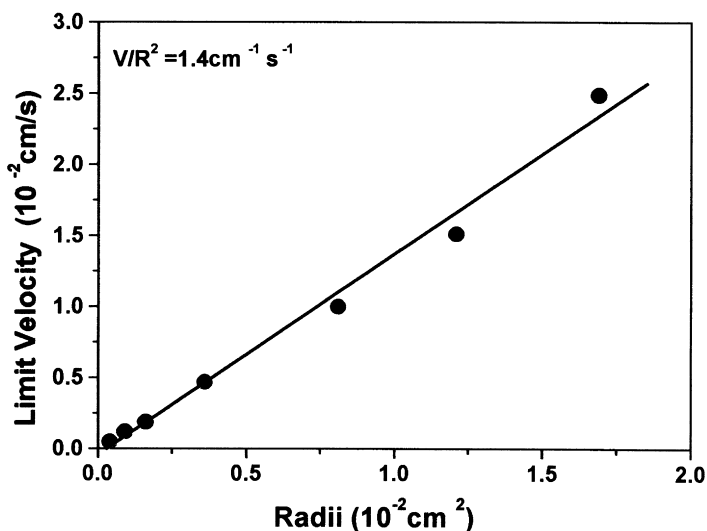


Fig. 8. Pellicle limit velocity dependence on the square of tube radius in pure furfuryl alcohol.

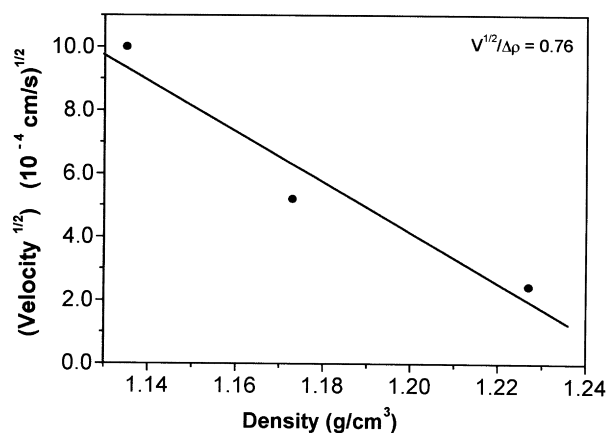


Fig. 9. Pellicle limit velocity dependence on the solution density measured in a 0.11 cm radius tube.

optical property resulting from oligomer pellicle organisation, it was lost. The Gaussian decomposition of each spectrum, the parameters of which are shown in Table 1, is also shown in the same figures.

The chemical analyses carried out in this study confirmed the attribution of the 360 nm band to dimers. The 460 and 406 nm optical absorption peaks, although related to the polymerisation reaction, were found not to be correlated with the conjugate chemical species of interest in this work. The other four absorption peaks were sensitive to the addition of triethylamine and are, therefore, attributed to conjugate oligomers. Table 1 shows the relative proportion among these conjugate compounds, assuming their optical absorption has the same oscillator strength. The most significant differences shown in Table 2 are the following. Homogeneous catalysis results in a more efficient production of oligomers with larger number of monomers,

as indicated by the 930 nm absorption band. The oligomer/dimer ratio is larger in heterogeneous catalysis. The high acid concentration on the surface does not produce oligomers with large numbers of monomers. This behaviour is attributed to several causes, i.e. the formation of oligomer clusters and their migration out of the high acid interfacial concentration, which decreases the reaction rate of larger oligomers; the arrangement of oligomers in the cluster may provide further protection for smaller oligomers; a combination of these causes contributes to control oligomer molecular size.

The simplest theoretical model to describe the dependence of the oligomer optical absorption band on its length is the electron in a unidimensional box [7,8]. According to this model, oligomer length is given by:

$$L_t^2 = \frac{h\lambda_{\max}^2(2N + 1)}{8mc} \quad (7)$$

where L_t is the theoretical length of the conjugate oligomer, N the number of π bonds in the chain, while the remaining symbols have their usual meaning. We tentatively assume that the optical absorption bands at 577, 650, 770 and 930 nm are due to 3, 5, 7 and 9 monomer oligomers, respectively. Calculated length L_t and its comparison with L_{real} is shown in Table 2. L_{real} was found by adding the length bonds, as follows:

$$L_{\text{real}} = [0.136N + 0.146(N + 1)] \text{ nm} \quad (8)$$

where 0.146 and 0.136 nm are the lengths of single and double bonds, respectively.

The above results show that oligomer length calculated from optical spectra is always smaller than the total bond length. The mismatch error is very close to that found for β carotene for the same type of calculation [9]. If the

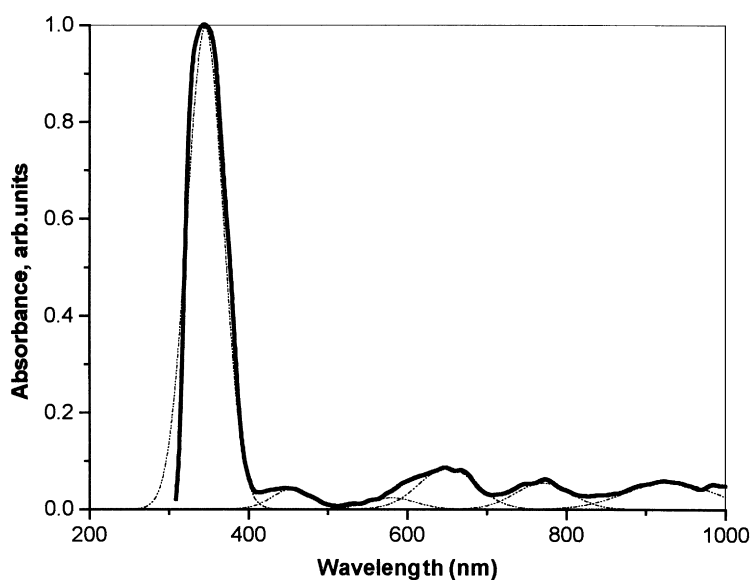


Fig. 10. Optical absorption spectrum of oligomer solution prepared by homogeneous catalysis. The full line represents the original spectrum while the dashed line represents its Gaussian decomposition.

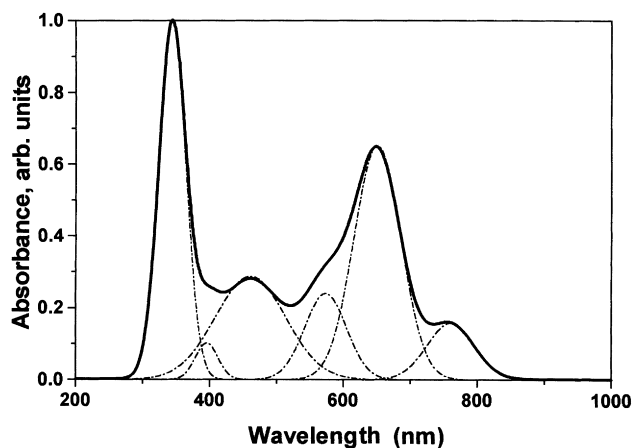


Fig. 11. Optical absorption spectrum of oligomers prepared by heterogeneous catalysis in a 0.11 cm radius glass tube. The full line represents the original spectrum while the dashed line represents its Gaussian decomposition.

attribution changes from 3–9 monomers to 5–11 monomers, the mismatch percentage in length increases from 50 to 100%. A good agreement was obtained by excluding oligomers with even numbers of monomers. The chemical instability of compounds having a hydroxyl radical associated with double bonds in the same carbon atom is a well-known subject [10,11]. Therefore, oligomers with even number of monomers cannot show the same conjugate bonds as do the odd oligomers.

3.3. Electrical measurements

The experimental arrangement of the FA film on the glass plate to take the electrical measurement is described in Section 2. Before FA was exposed to the HCl solution vapour, the electrical resistance was above 10 M Ω . At the beginning, exposure imparts a green colour to the FA film,

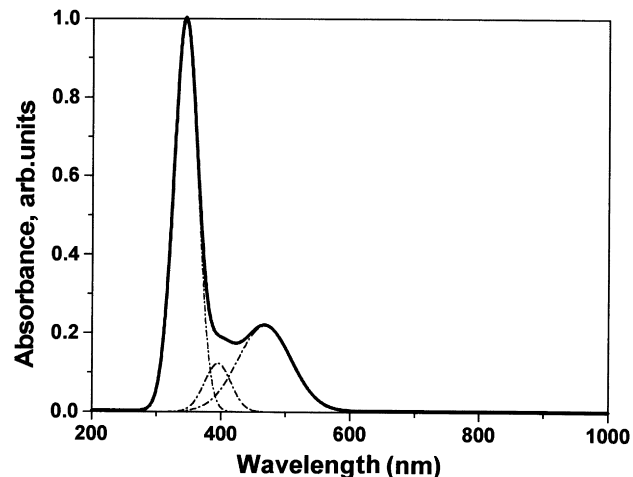


Fig. 13. Optical spectrum of the same solution shown in Fig. 11 after being neutralised by triethylamine.

Table 1

Peak intensity of each Gaussian component representing the optical absorption spectrum of each oligomer solution

Number of Mers	3	5	7	9
λ_{\max} (nm)	577.0	650.0	770.0	930.0
N	7	12	17	22
L_t (nm)	1.62	2.22	2.86	3.56
L_{real} (nm)	2.10	3.52	4.92	6.33
$(\frac{L_{\text{real}} - L_t}{L_{\text{real}}})$ (%)	23.0	37.0	42.0	44.0

with a simultaneous decrease of the electrical resistance to 420 Ω . Continued exposure made the film turn black, while the electrical resistance increased again to over 10 M Ω . The time interval of the low resistance indication was found to last not more than 30 s for more than 10 runs. The transient decrease observed in electrical resistance is attributed to

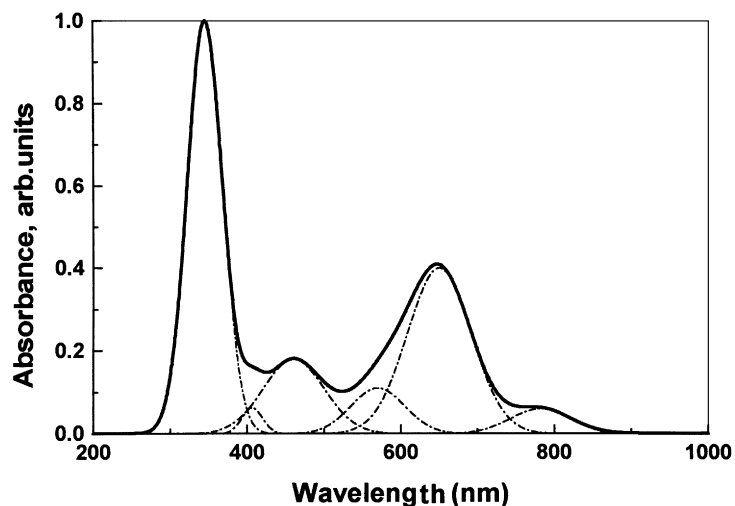


Fig. 12. Optical absorption spectrum of oligomers prepared by heterogeneous catalysis in a 0.085 cm radius glass tube. The full line represents the original spectrum while the dashed line represents its Gaussian decomposition.

Table 2
Peak intensity of the Gaussian components representing the optical absorption spectrum of each oligomer solution

λ_{\max}	0.085 cm glass tube radius	0.11 cm glass tube radius	Homogeneous catalysis, bubbling	Neutralised 0.085 cm solution
360	1.0	1.0	1.0	1.0
406	0.06	0.03	–	0.12
460	0.22	0.29	0.04	0.22
570	0.11	0.24	0.02	–
650	0.40	0.67	0.08	–
770	0.05	0.16	0.05	–
930	–	–	0.05	–

electronic conduction through the pellicle during the lifetime of conjugate oligomers. Ionic conduction that could have originated from a direct effect of the acid on the pellicle was discarded because of the transient nature of the effect observed. Further measurements are being taken to evaluate the time dependence of film conductivity.

4. Conclusions

Heterogeneous catalysis of FA polymerisation by HCl displays features not shown by homogeneous catalysis. The observed mechanical, optical and electrical properties result from the oligomers' bond conjugation character. The high acid concentration on the FA surface produces a high oligomer concentration, resulting in self-arranged oligomer aggregates or clusters. Because the 5-monomer oligomer concentration, measured by its optical absorption, is the highest, we concluded this is the critical size that makes cluster formation feasible. Clusters made of acid-doped conjugated oligomers are connected to each other, producing a porous electricity conducting pellicle. An electric current percolates through the connections between clusters.

The pellicle's falling motion would be impossible were it not for its porosity and the mechanical tension generated by attracting forces within the glass tube wall. In the absence of these forces, the pellicle would collapse, as in large FA surfaces or in a large radius (>0.27 cm) beaker, producing the pea-like black spots. Evaluation of the pellicle's mechanical strength showed a value 6 orders of magnitude lower than polyethylene and is, thus, compatible with the described porous pellicle.

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