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(54) **TRAITEMENT AU LASER DES LENTILLES CORNEENNES**

(54) **LASER CURING OF CONTACT LENS**

(57) A process for curing a photopolymerisable contact lens material comprising the step of irradiating the photopolymerisable contact lens material with laser radiation having a wavelength of between approximately 200nm to approximately 400 nm for a predetermined time period.

ABSTRACT

A process for curing a photopolymerisable contact lens material comprising the step of irradiating the photopolymerisable contact lens material with laser radiation having a wavelength of between approximately 200nm to approximately 400 nm for a predetermined time period.

The present invention relates to a process for curing a photopolymerisable contact lens material using coherent radiation.

5 Soft contact lenses are presently manufactured by injecting a hydrogel monomer mix into a mould which is rotated and exposed to ultraviolet radiation from a mercury lamp to photopolymerise the monomer mix. The hydrogel monomer mix consists of hydroxyethyl methacrylate, ethylene glycol dimethacrylate, ethylene glycol and a benzoin methyl ether photoinitiator. The 10 hydrogel monomer mix is usually exposed to the ultraviolet radiation from an array of mercury lamps for at least ten minutes to induce photopolymerisation after which the moulds are immersed in hot water to remove the ethylene glycol and other unpolymerised materials and to 15 release the lens from the mould. The polymerisation process must be carried out in the presence of an unreactive gas, for example nitrogen, in order to exclude oxygen which if present would inhibit the polymerisation.

20 A major disadvantage of the above process is that all extraneous radiations from the mercury lamps must be removed using optical filters. The optical filters and the mercury lamps must be water cooled both to filter

5 out infrared radiation and also to prevent overheating. Also, the mercury lamps have a limited lifetime and must be replaced periodically. Moreover, the ultraviolet radiation output from the mercury lamps decreases with operating time and therefore requires regular monitoring. In addition most of the energy of the lamps is discarded.

An object of the present invention is to mitigate the above disadvantages of curing contact lenses.

10 According to the invention there is provided a process for curing a photopolymerisable contact lens material comprising the step of irradiating the photopolymerisable contact lens material with laser radiation having a wavelength of between approximately 15 200nm to approximately 400nm, for a predetermined time period.

20 Preferably the contact lens material comprises a hydrogel monomer mix. The hydrogel monomer mix preferably comprises hydroxyethyl methacrylate, ethylene glycol dimethacrylate, ethylene glycol and a benzoin methyl ether photoinitiator.

Further preferably, the contact lens material is rotated in a mould during laser irradiation.

25 More preferably, the contact lens material is irradiated in an oxygen free environment. Further preferably, the contact lens material is irradiated in the presence of a gas unreactive relative to the contact lens material under the conditions of curing. The unreactive gas is preferably argon, or nitrogen.

5 Suitable lasers preferably comprise the excimer
lasers (XeF, XeCl and KrF operating at 351nm, 308nm and
248nm respectively) the nitrogen laser operating at
337nm, solid state lasers operating at approximately
355nm, and the ultraviolet output radiation of the Argon
and Krypton ion lasers.

10 The selected lasers operate at suitable pulse energy
levels and repetition rates to achieve
photopolymerisation of the contact lens material in a
reasonably short time period.

15 The advantages of the invention are that there is
improved control and shorter polymerisation times are
achieved, and there is less maintenance required of the
laser equipment than for mercury lamps and attendant
technology. In addition, the use of a laser enables
automation of the process to be achieved easily and also
there is no cooling or optical filtering equipment
necessary as with mercury lamps.

20 Embodiments of the invention will now be described,
by way of example, with reference to the accompanying
drawings, in which:-

Figure 1 is a diagrammatic view of an apparatus for
carrying out the process according to the invention;

25 Figure 2 is a diagrammatic view of an apparatus for
monitoring the amount of photopolymerisation in a sample
of contact lens material;

Figure 3a, 3b and 3c are graphs showing the change
in an infrared spectrum during photopolymerisation;

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Figure 4 is a graph showing the curing curve of a contact lens material irradiated as described in example 1;

5 Figure 5 is a graph showing the curing curve of a contact lens material irradiated as described in example 2;

Figure 6 is a graph showing curing curves of a contact lens material irradiated as described in example 3;

10 Figure 7 is a graph showing a curing curve of a contact lens material irradiated as described in example 4;

15 Figure 8 is a graph showing curing curves of a contact lens material irradiated as described in example 5;

Figure 9 is a graph showing a curing curve of a contact lens material irradiated as described in example 6;

20 Figure 10 is a graph showing curing curves of a contact lens material irradiated as described in example 7; and

Figure 11 shows the absorption spectrum of a cured sample of contact lens material.

25 Referring now to Figure 1, there is shown therein an apparatus generally indicated at 10 for carrying out the process according to the invention. A conventional soft contact lens material 11 in the form of a hydrogel monomer mix is placed in a rotatable mould 12 which can

5 be rotated at a suitable speed for example 350rpm as is
known in the art. The lens material 11 and mould 12 are
located in a housing 13 defining a substantially oxygen
free chamber 14. The chamber 14 has an unreactive gas
such as nitrogen or argon introduced therein. The mould
12 containing the contact lens material 11 is rotated at
a suitable speed so as to form an inner concave surface
on the eventual lens. The ultraviolet laser 15 is then
operated producing a laser beam 20 which is directed onto
10 the lens material 11 at a suitable pulse energy level and
repetition rate and for a sufficient period of time to
polymerise the contact lens material 11. Clearly, the
laser beam 20 is of a sufficient width to cover the lens
material 11 or it may be off-set from the axis of
15 rotation to enable all the lens material to be
irradiated.

The degree of polymerisation of the contact lens
material 11 can be continuously monitored using the
arrangement shown in Figure 2, or a similar arrangement.
20 As shown, the contact lens material 11 is placed on a
NaCl substrate 16 in a chamber 14' defined by a housing
13'. The chamber 14' is oxygen free and argon gas is
introduced via a conduit 17. An ultraviolet laser beam
20' is directed into the chamber 14' via a window 18 and
25 is reflected by a quartz prism 19 and directed onto the
contact lens material 11. The substrate 16 may be
rotated in conventional manner.

30 An infrared light beam 21 is directed through the
contact lens material 11 and the infrared beam 21'
transmitted by the sample 11 is monitored by an infrared
spectrometer 22. A reference infrared light beam 23 is
also directed into the chamber 14' and the transmitted
reference beam 23' is also monitored by the spectrometer

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22. The output spectrum of the spectrometer 22 demonstrating the progressive cure of the lens material 11 is shown in Figures 3a, 3b and 3c. The spectrometer 22 compares the sample beam 21' with the reference beam 23' and provides the IR absorbance spectrum of the sample material 11 as shown in each of Figures 3a, 3b and 3c. In Figures 3a, 3b and 3c the absorbance peak B is the carbon oxygen c=O absorbance peak at 1720 cm^{-1} and the absorbance peak A is the carbon carbon c=c absorbance at peak 1640 cm^{-1} . Figure 3a provides the absorbance spectrum prior to any polymerisation of the sample material 11 and thus the carbon carbon, c=c absorbance peak is at a maximum as shown by A_0 . Figure 3b represents the absorbance spectrum at an intermediate stage of polymerisation of the sample material 11 and thus the carbon carbon, c=c absorbance peak A_i has reduced in size. Figure 3c represents the absorbance spectrum after a time t when almost complete polymerisation of the sample 11 has occurred and thus the absorbance peak A has diminished in size as shown to A_t . It will be clear that the size of the carbon oxygen c=O absorbance peak remains constant as this is not affected by the polymerisation of the sample contact lens material 11.

As is known in the art, due to the absorbance by the monomer the amount of infrared absorption decreases with polymerisation of a hydrogel monomer mix, and Figure 3a illustrates no polymerisation, Figure 3b illustrates a moderate amount of polymerisation and Figure 3c illustrates almost complete transmission of the infrared sample beam 21' at 1640 cm^{-1} and thus almost complete polymerisation of the contact lens material 11'.

EXAMPLE 1

5 A sample of typically 10 micro-litres of
conventional hydrogel monomer mix was spread on a CaF
substrate and exposed in an oxygen free chamber to a XeF
excimer laser emitting laser beam of 351nm pulses at a
4Hz repetition rate and with a pulse energy of 35mJ.
The degree of polymerisation was monitored periodically
using the infrared technique described above. The
10 results are shown in Figure 4 which is a graph
illustrating fraction polymerised against time in
minutes. As shown, the sample was approximately 85%
polymerised after six minutes.

EXAMPLE 2

15 A sample of 10 micro-litres of conventional hydrogel
monomer mix was spread on a CaF substrate and exposed in
an oxygen free chamber to an N₂ laser emitting a laser
beam of 337nm pulses at a 4Hz repetition frequency and
with a pulse energy of 0.3mJ. The degree of
polymerisation was monitored periodically using the
20 infrared technique described above. The results are
shown in Figure 5 which is a graph similar to that of
Figure 4. As shown, the sample was approximately 85%
polymerised after three minutes and almost completely
polymerised after six minutes.

25 EXAMPLE 3

A sample of 10 micro-litres of conventional hydrogel
monomer mix was spread on a NaCl substrate and exposed in
an oxygen free chamber to an N₂ laser emitting a laser
beam of 337nm pulses at 100Hz repetition frequency and
30 with a pulse energy of 0.7mJ. The degree of

polymerisation was monitored continuously using the infrared technique described above. A similar sample of monomer mix was similarly exposed to the laser irradiation but with the N₂ laser operating at 100Hz repetition frequency but with a pulse energy of 0.3mJ. The results are shown in Figure 6 which is a graph similar to that in Figure 5. As shown, 0.7mJ pulses appear to be the least energy required to achieve over 90% curing in two minutes.

10 EXAMPLE 4

15 A sample of 10 micro-litres of conventional hydrogel monomer mix was spread on a NaCl substrate and exposed in an oxygen free chamber to an N₂ laser emitting a laser beam of 337nm pulses at 10Hz repetition frequency and with a pulse energy of 0.75mJ. The degree of polymerisation was monitored continuously using the infrared technique described above. The results are shown in Figure 7 from which it will be observed that 90% curing was achieved in five minutes at which time the laser was switched off however, the curing continued reaching 100% cure in about 1.5 hours in the absence of further irradiation.

EXAMPLE 5

25 A sample of 10 micro-litres of conventional hydrogel monomer mix was spread on a NaCl substrate and exposed in an oxygen free chamber to an N₂ laser emitting a laser beam of 337nm pulses at 100Hz repetition frequency and with a pulse energy of 0.7mJ. The degree of polymerisation was monitored continuously using the infrared technique described above. A similar sample of monomer mix was also spread on an NaCl substrate and was exposed in an oxygen free environment to an N₂ laser

emitting a laser beam of 337 nm pulses at 10Hz repetition frequency and with a pulse energy of 0.75mJ. The sample was monitored and the results are shown in Figure 8 from which it will be noted that at the lower pulse rate of 10Hz the curing rate was slower. The lower rate of 10Hz simulates the effect which would be obtained if say a laser operating at 100Hz repetition rate was used to sequentially scan ten samples.

EXAMPLE 6

A sample of 10 micro-litres of conventional hydrogel monomer mix was spread on a NaCl substrate and exposed in an oxygen free chamber to an XeF excimer laser with 4mJ pulses at 100Hz repetition rate. The laser was intermittently switched on and off and the degree of polymerisation was monitored continuously using the infrared technique described above. The results are shown in Figure 9 from which it will be noted that curing clearly continues after the laser has been turned off (the value of F rises from 0.4 to 0.6 during the two minutes after the initial laser irradiation phase). Once the fraction cured reaches about 0.9 however, the presence of the laser beam appears to have only a minimal affect on the curing rate.

EXAMPLE 7

A sample of 10 micro-litres of conventional hydrogel monomer mix was spread on a NaCl substrate and exposed in an oxygen free chamber to an XeF excimer laser with 0.35mJ pulses at 100Hz repetition rate. A similar sample was also spread on a NaCl substrate and exposed in an oxygen free chamber to an XeF excimer laser with 25mJ pulses at 10Hz repetition rate. The degree of

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polymerisation was monitored continuously and the results are shown in Figure 10. The upper trace at the 100Hz repetition rate has an average irradiated power of 35mW yet it has a faster initial cure rate than the 10Hz trace which has an average power of 250mW. It appears that a higher repetition rate produces a higher initial cure rate.

EXAMPLE 8

A sample of 26 micro-litres of conventional hydrogel monomer mix was deposited in a contact lens mould (see Figure 1) rotating at a speed of 350 rpm. The sample was exposed in an argon atmosphere to an N₂ laser beam (337nm) operating at 100Hz repetition rate with a pulse energy of 3mJ. After 2 minutes the mould was removed from the argon atmosphere, and soaked in hot water after which the polymerised contact lens was removed. The contact lens was free from visual blemishes and judged to be suitable for use.

The technique for monitoring the degree of polymerisation of a sample of contact lens material during laser irradiation can normally only be carried out on thin samples of lens material. The technique cannot be carried out successfully on samples of contact lens material which are of sufficient volume to produce an actual contact lens as such volumes are too great to enable a quantitative measurement of the transmission spectrum of an infrared light beam. The results of the tests on the small volumes in examples 1 to 7 clearly demonstrate the parameters for successful photopolymerisation of a conventional contact lens material.

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5 In Figure 11 there is shown the absorption spectrum
of a 1.4mm thick cured sample of a conventional hydrogel
contact lens material. From this curve the optimum
curing laser wavelengths are determined. As shown, laser
light above 380nm is impractical since only a small
fraction of it will be absorbed (8% over a 1mm depth).
On the shorter wavelength side, the material absorbs
strongly around 300nm and below and so only very thin
layers could be cured with these wavelengths. It appears
10 that the optimum laser wavelengths for
photopolymerisation is within a range of approximately
300nm to approximately 380nm and so the most useful
lasers are likely to be the XeCl and XeF excimer lasers
(308 and 351nm respectively) and the N₂ laser (337nm).

15 The invention is not limited to the embodiments
described herein which maybe modified or varied
without departing from the scope of the invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for curing a photopolymerisable contact lens material comprising the step of irradiating the photopolymerisable contact lens material with pulsed laser radiation having a wavelength of between approximately 200nm to approximately 400nm for a predetermined time period.

2. A process as claimed in Claim 1, wherein the laser radiation has a wavelength of between approximately 300nm to approximately 380nm.

3. A process as claimed in Claim 1, wherein the contact lens material is irradiated in an oxygen free environment.

4. A process as claimed in Claim 2, wherein the contact lens material is irradiated in an oxygen free environment.

5. A process as claimed in claim 1, wherein the contact lens material is irradiated in the presence of a gas unreactive relative to the contact lens material under the conditions of curing.

6. A process as claimed in Claim 2, wherein the contact lens material is irradiated in the presence of a gas unreactive relative to the contact lens material under the conditions of curing.

7. A process as claimed in Claim 5, wherein the gas is argon or nitrogen.

8. A process as claimed in any preceding claim, wherein the contact lens material is rotated in a mould during irradiation.

9. A process as claimed in any preceding claim wherein the laser operates at selected pulse energy levels and repetition rates to achieve photopolymerisation of the contact lens material in a reasonably short time period.

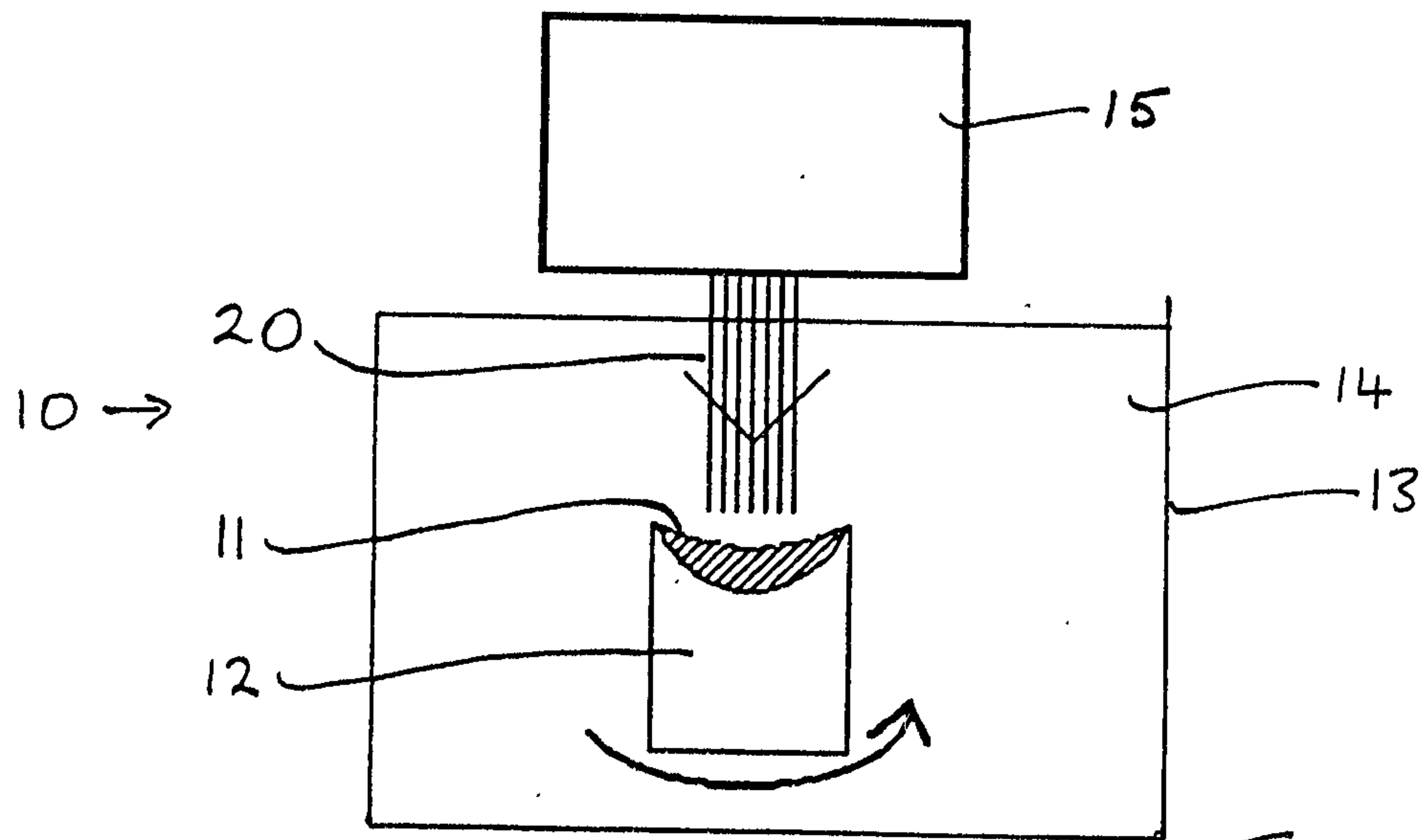


Figure 1

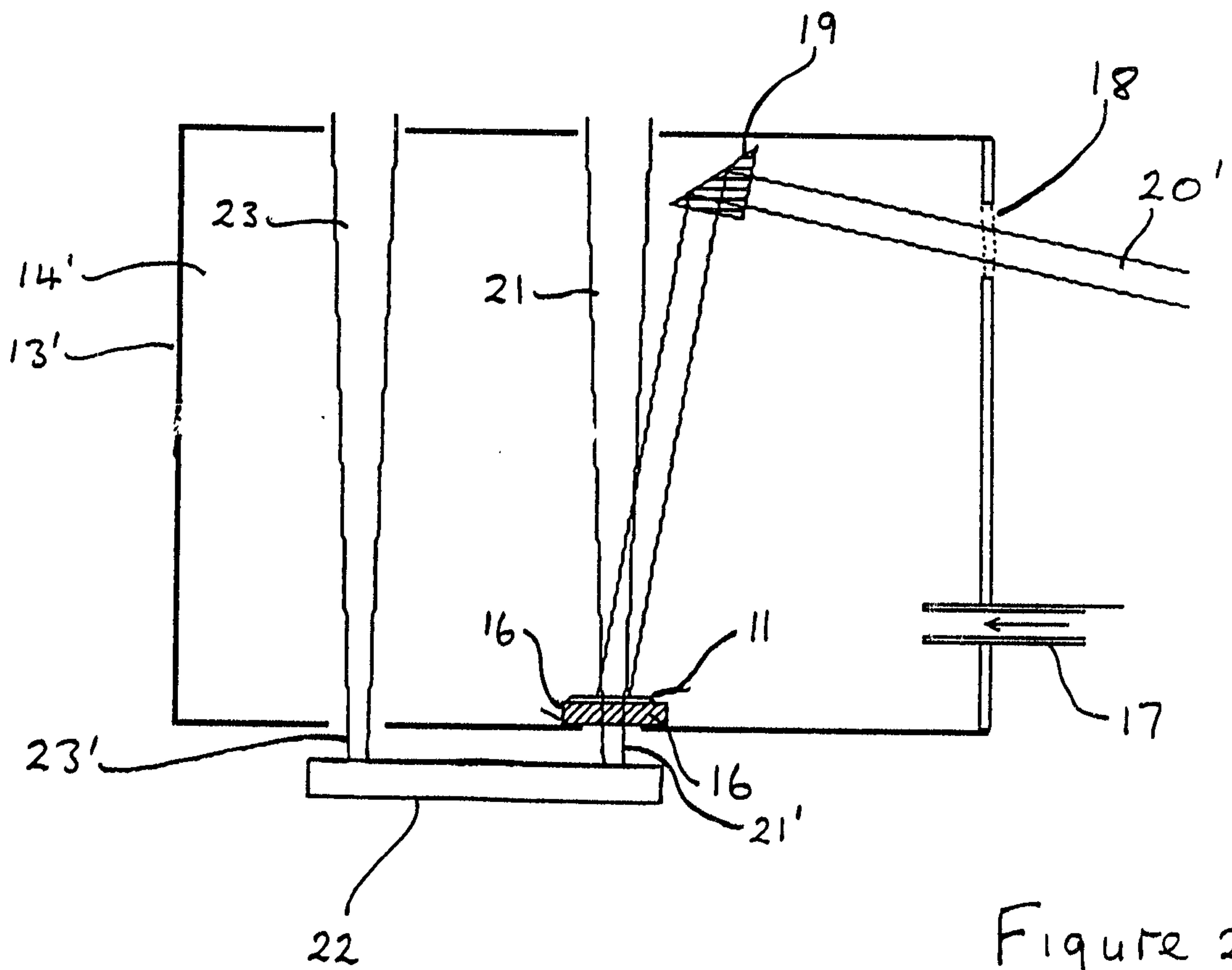
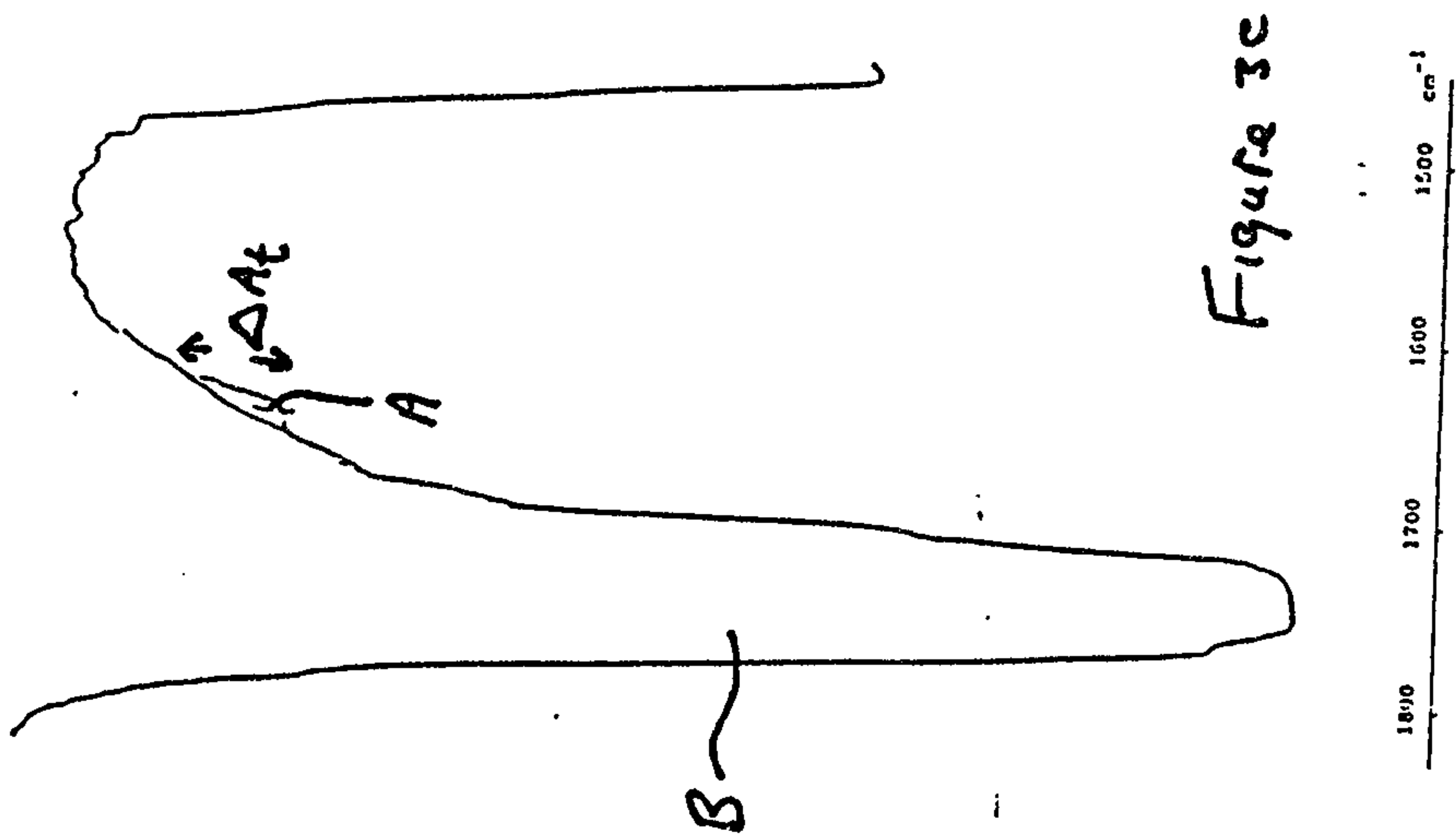
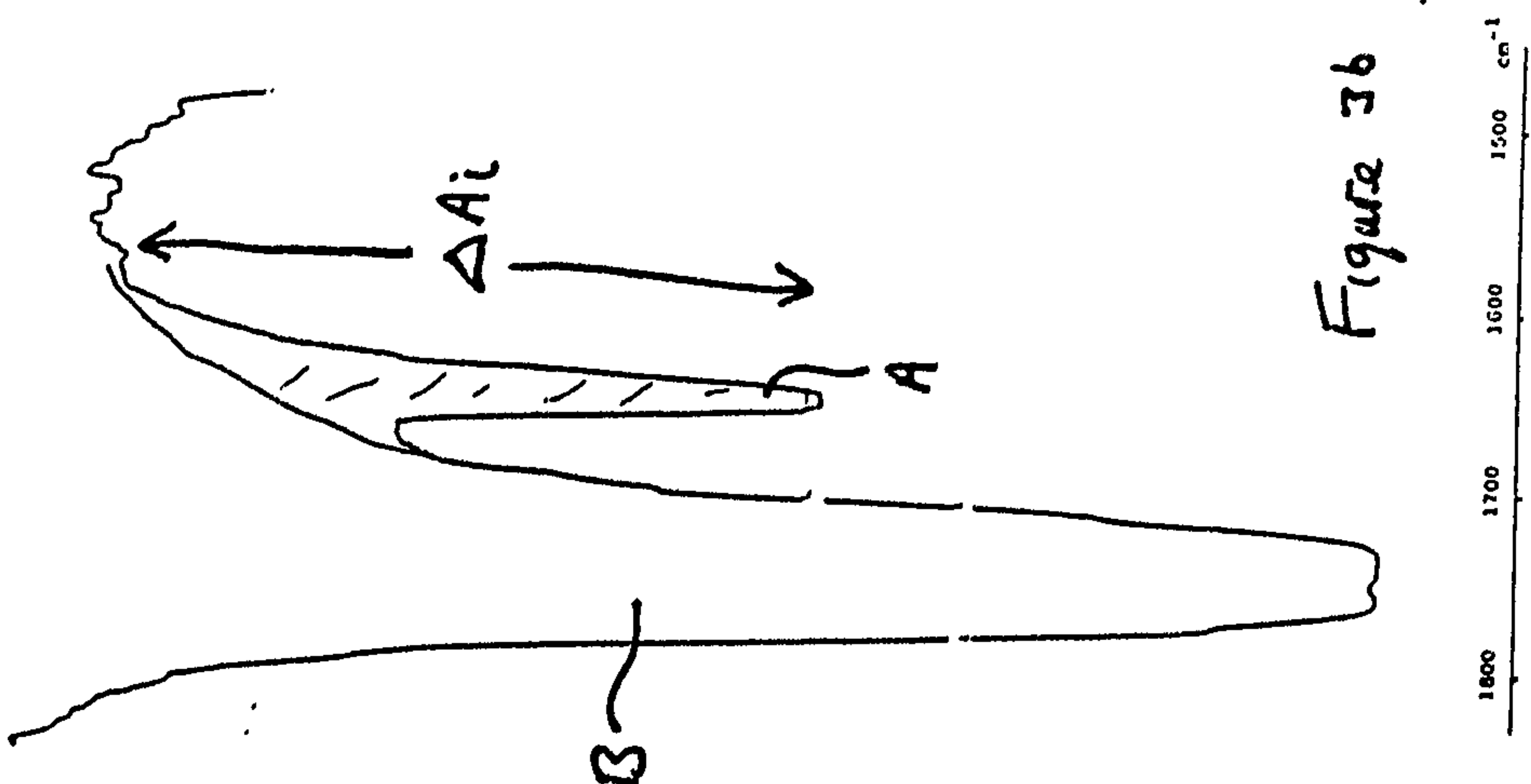
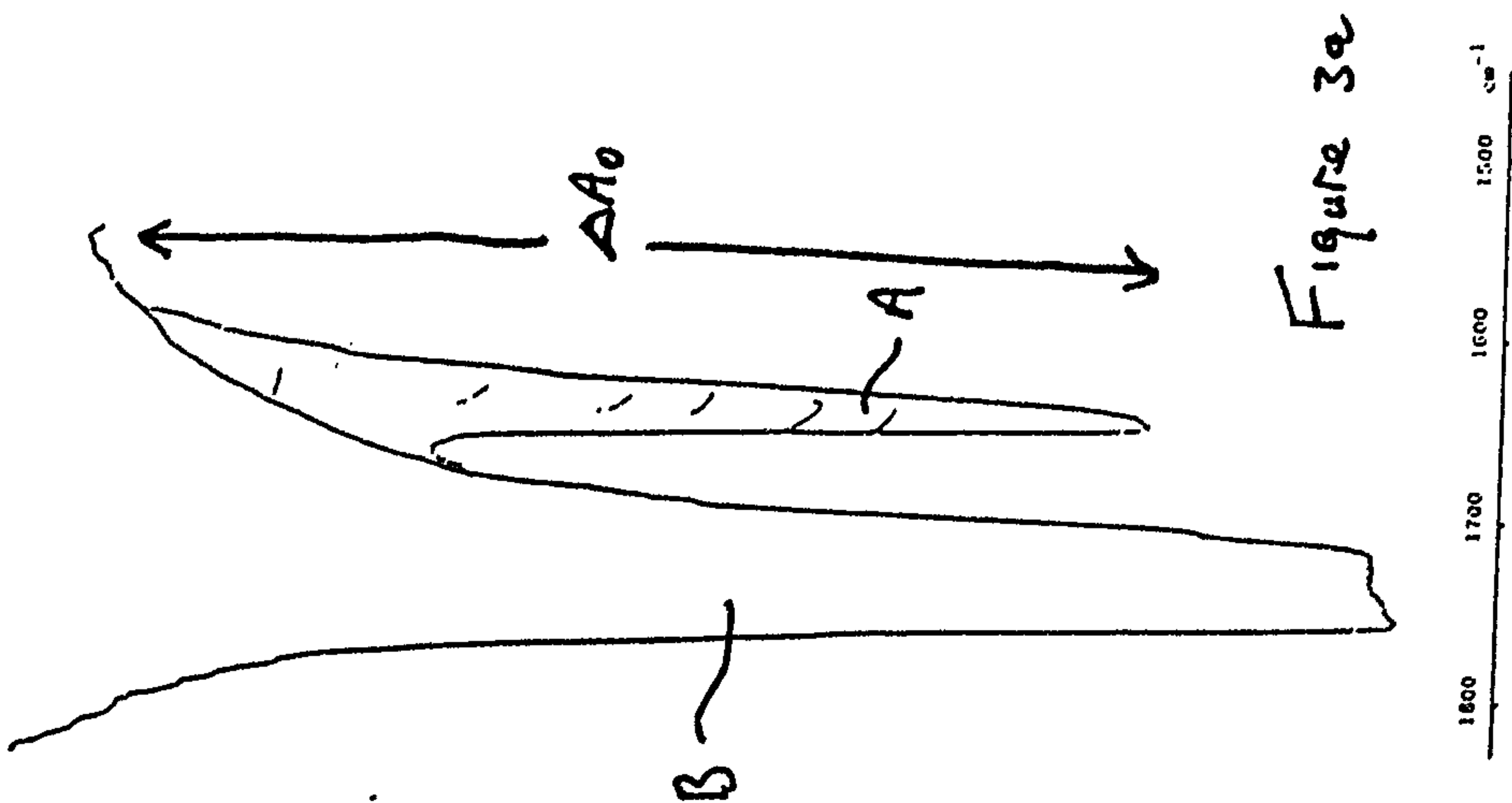


Figure 2.



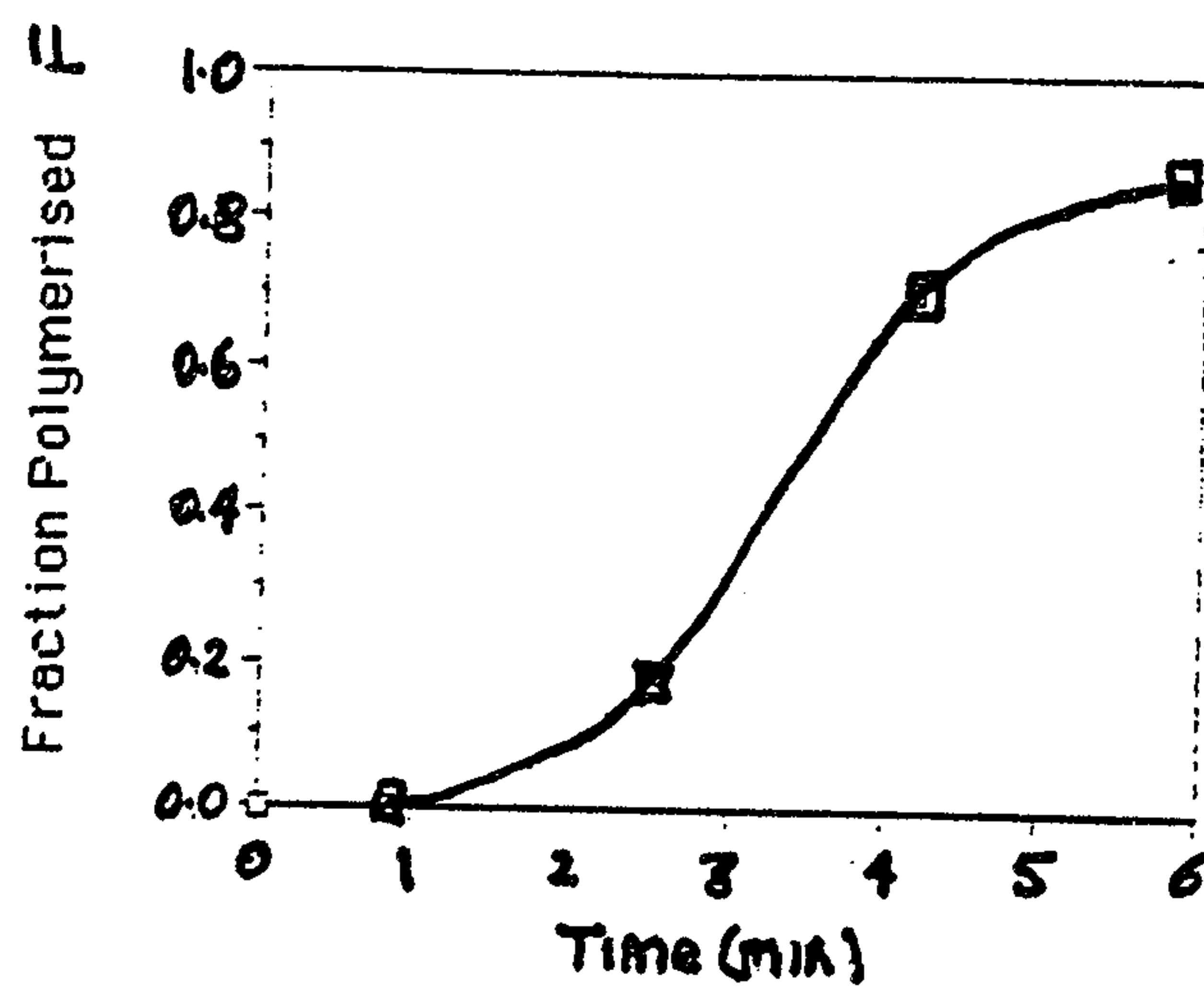


Figure 4

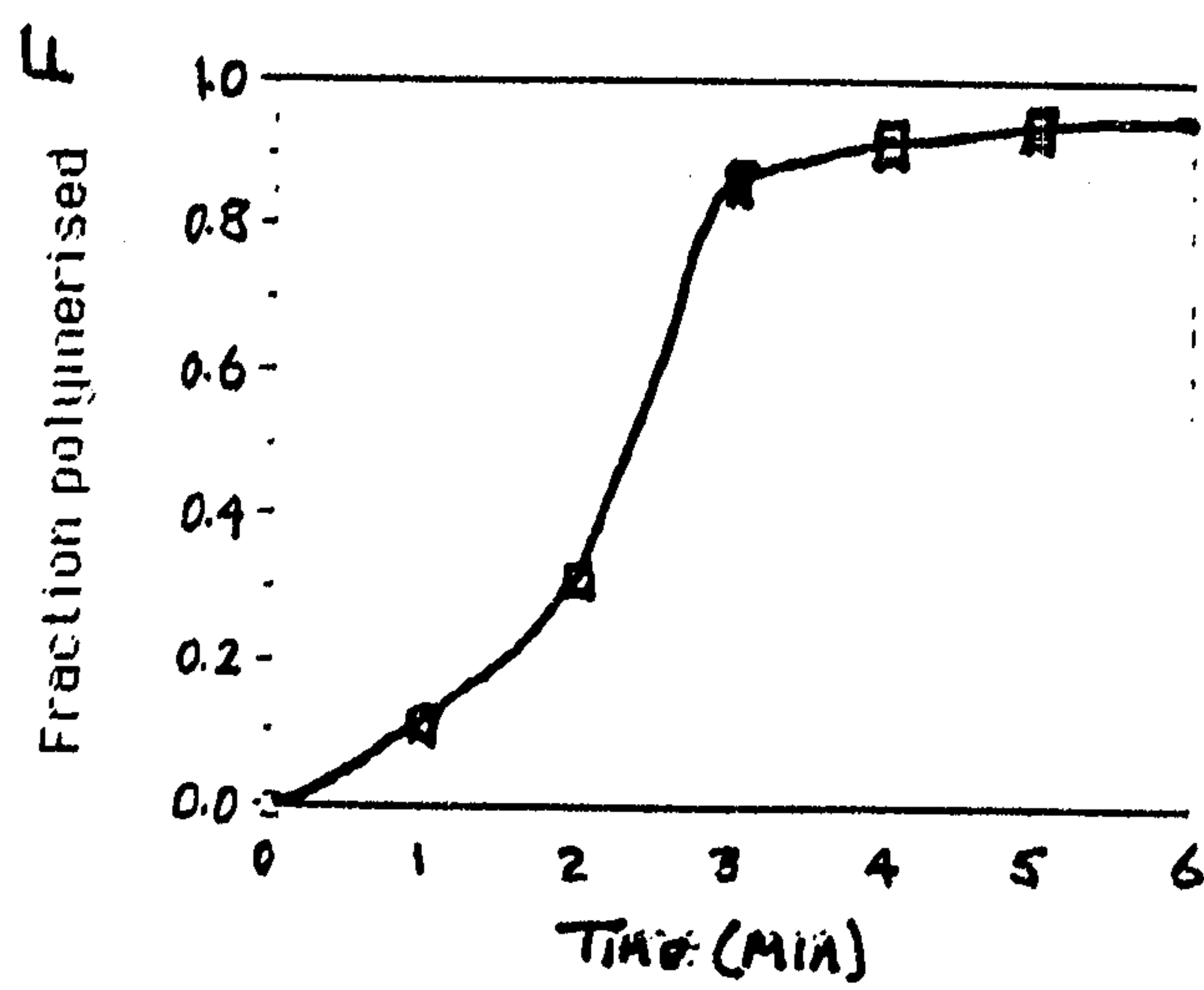


Figure 5

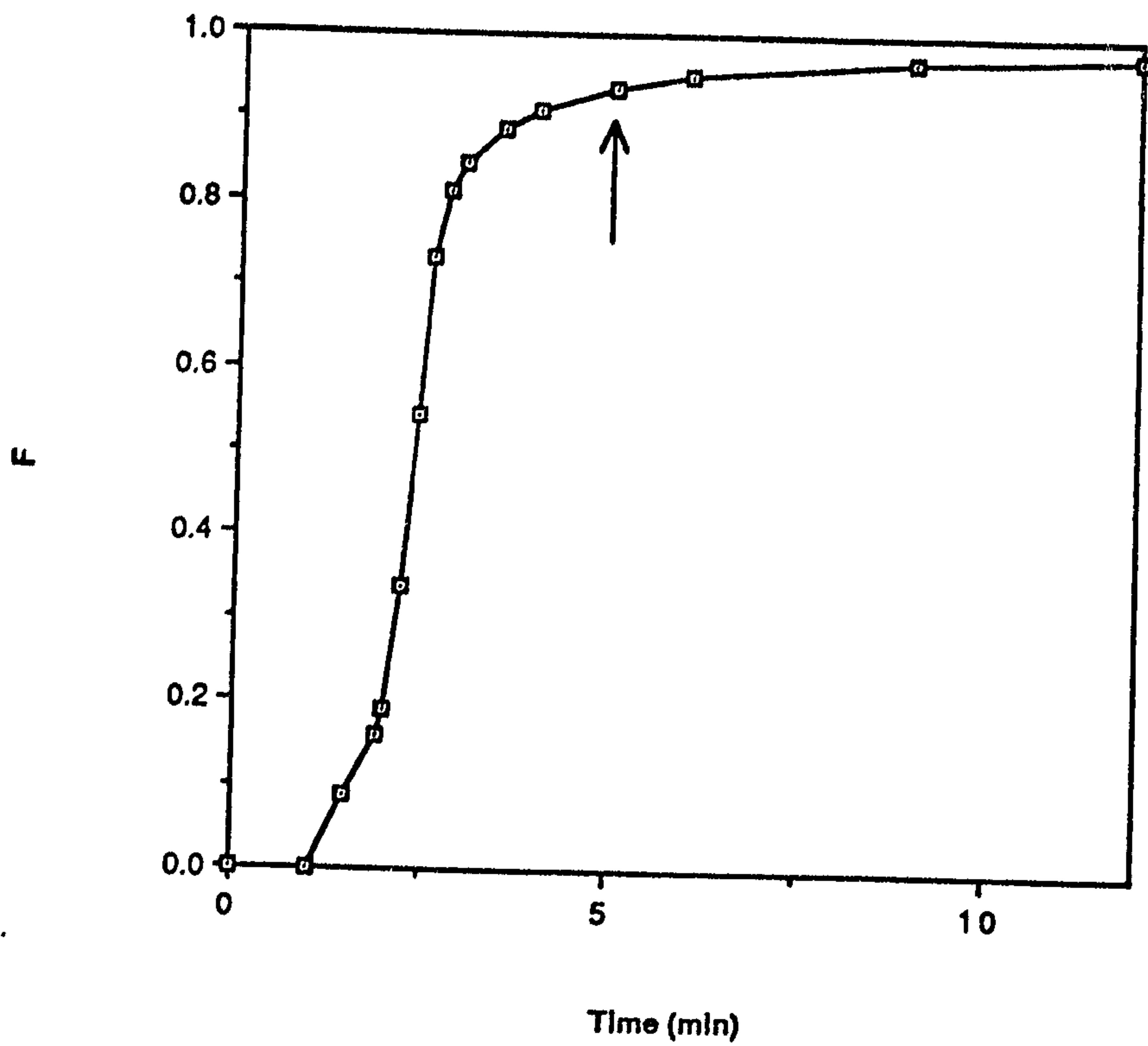
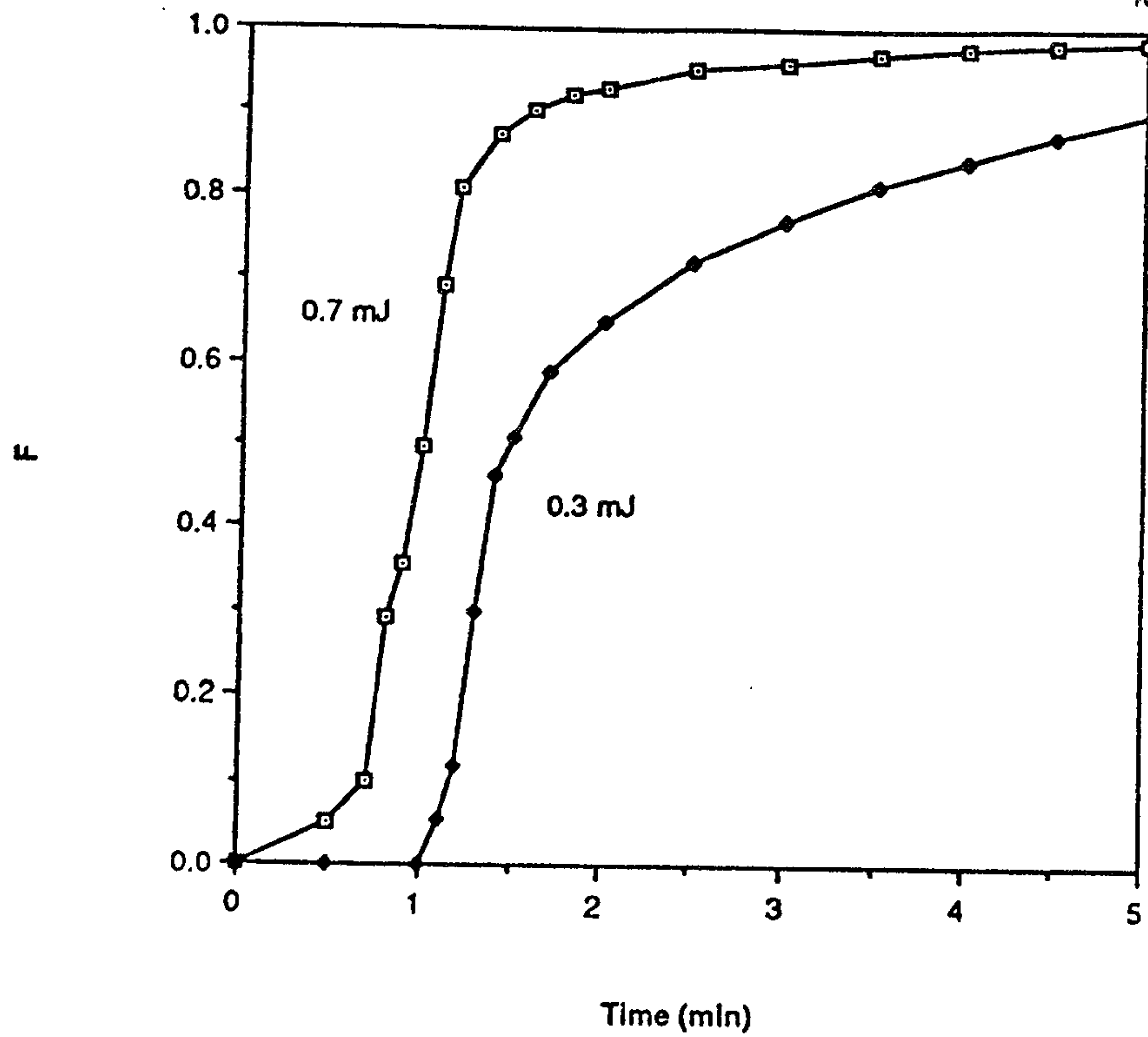
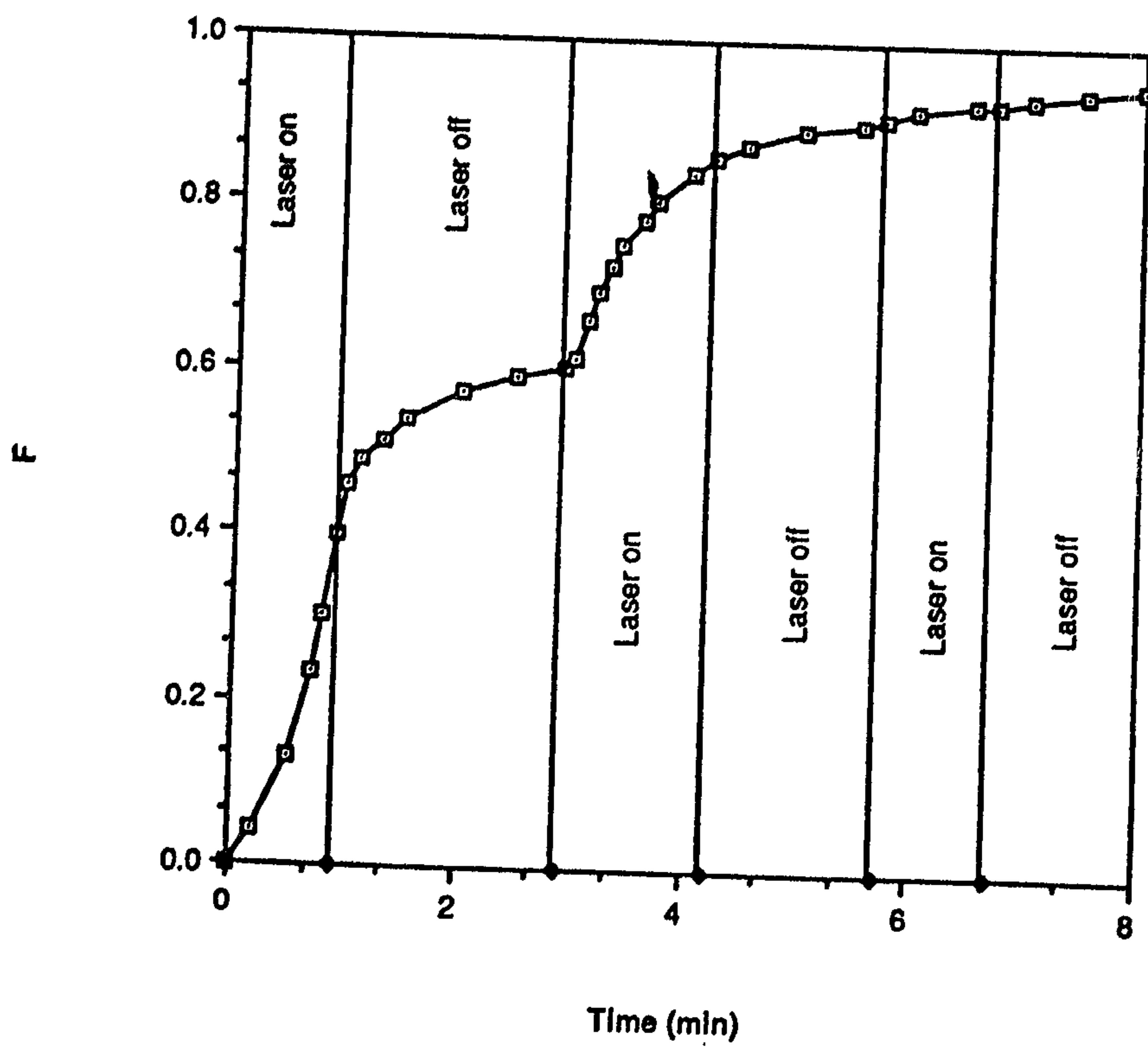
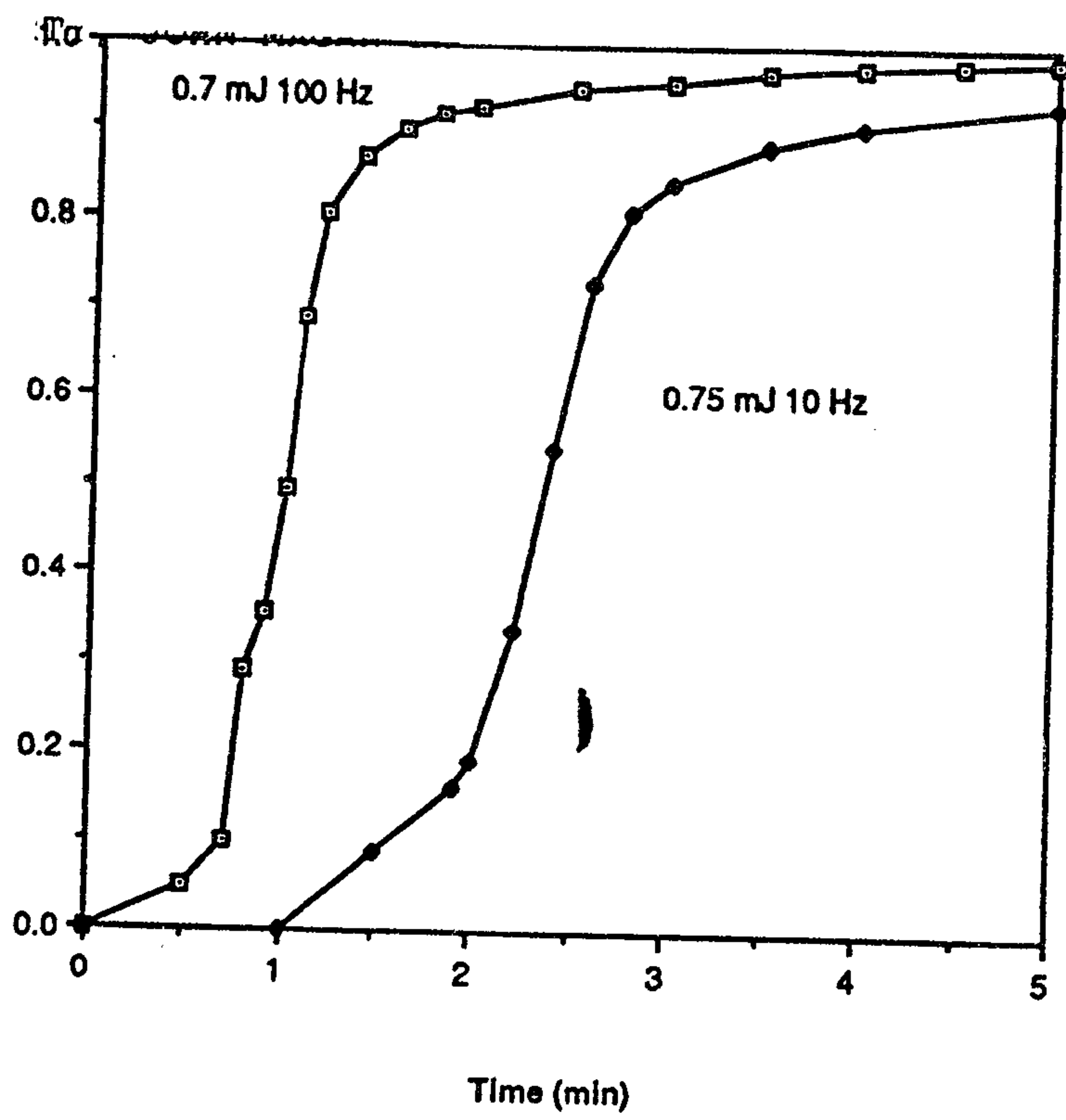
Figure 6
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Figure 7



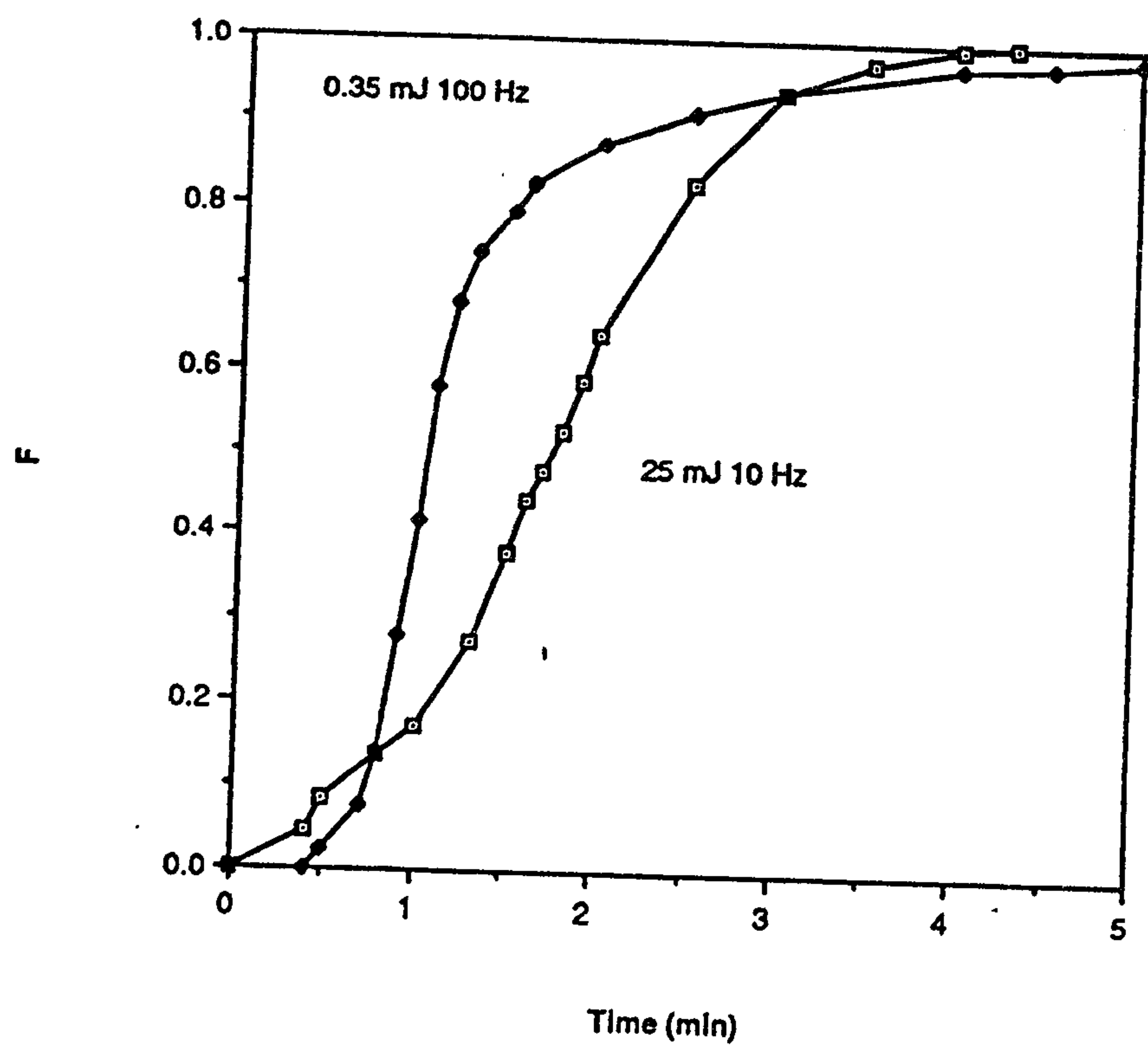


Figure 10.

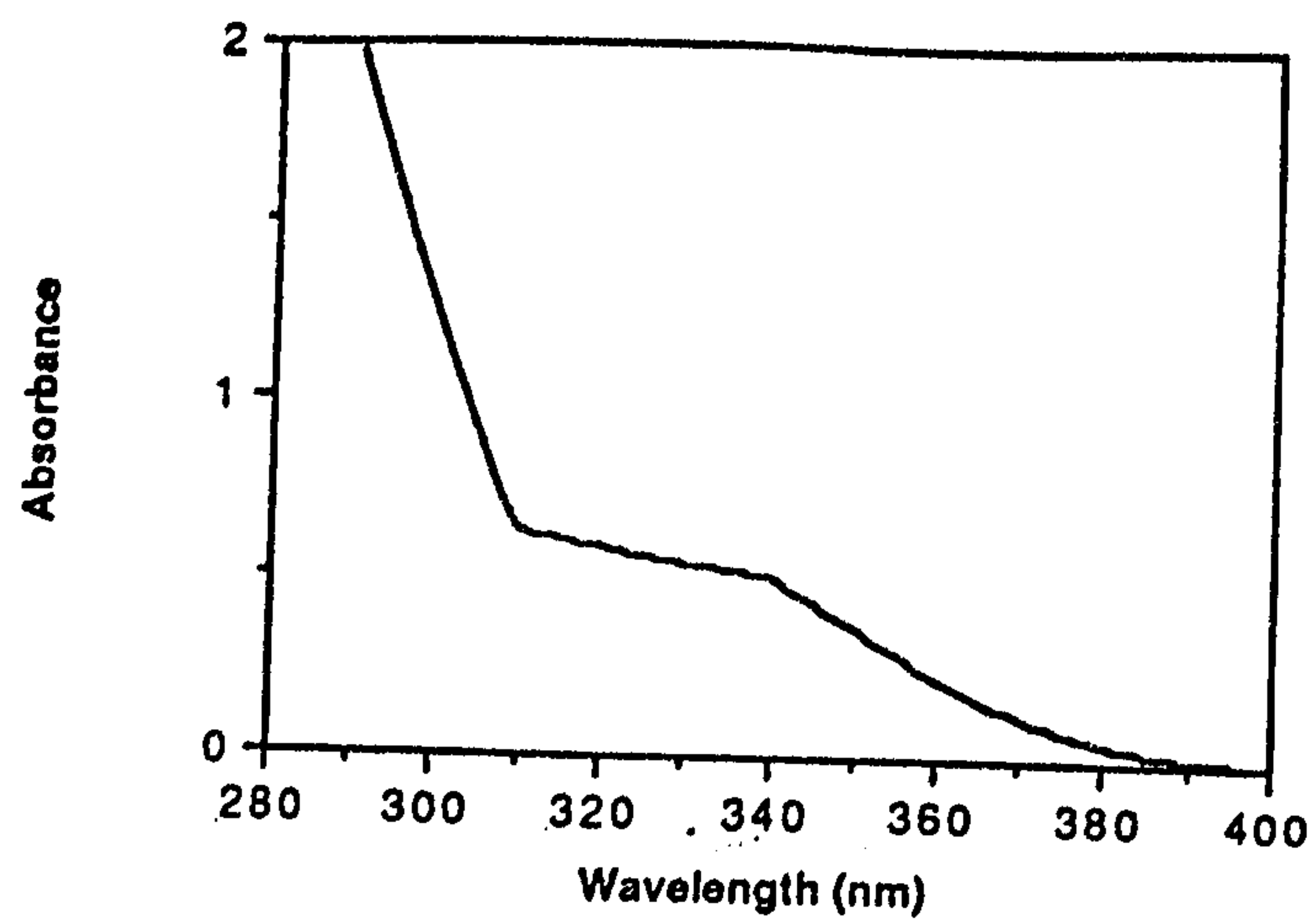


Figure 11