

Visualization of interfacial urethane polymerizations by means of a new microstage reactor

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Mixing activated polymerizations, such as RIM urethane polymerizations, may evolve from an imperfectly mixed state; this can drastically modify the characteristics of the polymer formed. Here we focus on the basic building block of the unmixed state: a single interface between reactive monomers. We present a reactor which allows the visualization of the interface by using an optical microscope and use it to document a variety of phenomena for two and three component urethane polymerizations: (1) the interface may or may not be stable, producing fingering, roll cells, or spontaneous generation of interfacial area, (2) different types of domains (e.g. crystalline or phase-separated) may be formed on opposite sides of the interface, and (3) hard and soft domains may be segregated for the three component polymerization due to diffusional effects.

(Keywords: interfacial polymerization; instabilities; polyurethane reactions)

INTRODUCTION

Traditionally, three-component urethane polymerizations have been treated as well mixed (i.e. molecularly mixed) homogeneous reactions producing random block copolymers. However, due to imperfect mixing¹ or monomer incompatibility², these reactions, as well as other mixing activated polymerizations, may evolve from an imperfectly mixed state. Thus, the polymerization occurs by diffusion and reaction between essentially pure monomer regions. Such effects were invoked in order to explain product segregation in urethane polymerizations¹⁻³.

The unmixed initial state can be studied theoretically and experimentally. The simplest mathematical treatment which captures the essential aspects of the problem involves a periodic array of striations of monomers with the reaction initially occurring at the interfaces. Such a configuration is analysed in detail by Fields and Ottino^{4a,b} and leads to several unexpected results, such as (1) hard/soft/hard/soft product layers being formed solely due to diffusion-reaction interactions, and (2) an intermediate level of mixedness yielding the highest peak in the spatial molecular weight profile. In this article we consider the natural companion of the modelling results: an experiment focusing on the interfacial region between two reactive monomers. We present the design and application of a microreactor which allows the visualization, with an optical microscope, of a single interface between two reactive monomer phases. Several interesting phenomena are revealed which have implications on previous interpretive morphological work on RIM samples, mathematical modelling, and practical importance, since it is found that various

formulations promote interfacial instabilities which lead to enhanced mixing.

There have been many studies in which investigators have created interfaces between liquids to study mass transport, reactions and interfacial phenomena, but only a few will be mentioned here. In the simplest case, a droplet of one material may be placed in a large region of another fluid. This has been done using a syringe or pipet to form the droplet⁵⁻⁷ to study solute transfer between aqueous and organic phases. These investigators noted oscillations, pulsations and rippling of the droplets, and found that these were dependent on the direction of transfer. Other authors noted that a spontaneous emulsion could be formed when mass was transferred between macroscopic layers of aqueous and organic materials⁸⁻¹⁰. For example, Ward and Brooks¹¹ studied diffusion across organic/aqueous interfaces in a cylindrical optical cell using refractive index to measure concentrations in the neighbourhood of the interface. Work done in stirred transfer cells on aqueous/organic mass transport reported^{12,13} the occurrence of interfacial instabilities, spontaneous emulsification and drop formation. Cho and Ranz¹⁴ studied interfacial turbulence by forming an interface between two reactive liquid phases. The interface was formed by layering the phases in an optical cell using syringes, and a Schlieren method was used to study the diffusion-reaction process and the influence of interfacial turbulence on acid-base reactions. Several other works¹⁵⁻¹⁷ used a similar vertical optical cell and a Schlieren technique to study transport between aqueous and organic liquids. Cellular eddies, streaming convection and emulsification were noted.

All of the above works pertain to the case of low molecular weight liquids with mass transport or simple reactions. When compared with reactions between viscous monomers, these systems present little difficulty in forming a controlled interface. In an interfacial

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polymerization, a polymer layer forms quickly between the monomers which does not allow much adjustment of the interface. This means that the experimental apparatus for such systems must be constructed in such a way that the initial contact of the monomers provides a controlled interface.

Even though there has been a lot of work done on interfacial polymerizations^{18,19}, there has been little work done similar to that described above for low molecular weight liquids. This is possibly due to the lack of a suitable experimental apparatus. In the context of polymerizations between reactive monomers, Ranz²⁰ suggested that droplets of the monomers could be placed on a microscope slide next to each other and a coverglass attached to the microscope objective could be used to squeeze the droplets, forming an interface between them. Ottino *et al.*²¹ constructed a different device to accomplish the same goal; droplets were injected into the 340 μm gap between fixed microscope cover glasses via syringe needles attached to micropipets. The interface was formed at the point where the monomer droplets touched. A crosslinking polyurethane system was studied with an optical microscope and instabilities were noted. However, the results were inconclusive.

APPARATUS DESIGN

The minimum experimental requirements are:

(1) A single reproducible interface must be formed which is nearly planar, stationary, and as free as possible from end effects.

(2) The apparatus allows viewing of the interface with an optical microscope since effects of interest would be concentrated in a 100 μm wide region in each side of the interface.

(3) The experimental procedure is reasonably simple and quick so that experiments can be performed in a relatively short period of time.

(4) The temperature of the system can be controlled over the range: 20°C to 100°C.

The choice for contacting the reactants was the squeezing method, similar in concept to that envisioned by Ranz²⁰. By confining the fluids between parallel glass plates, the fluids are contained in a region essentially isolated from the environment. This is important for chemical systems which are moisture sensitive (for example, urethanes). Also, if the interface is perpendicular to the surfaces of the plates and has small curvature, the interface may be viewed in projection as a single line. If microscope slides are used as the glass plates, they could be replaced after each experiment. This would be particularly useful for polymerizations since the apparatus would not require tedious cleaning between experiments. Instead of using the microscope objective to control the relative movement of the parallel plates, as suggested by Ranz²⁰, an independent set of controls was desired. That way, the squeezing and focusing controls could be decoupled. A droplet of each reactant could then be placed on one (the bottom) microscope slide and a vertical interface formed by squeezing the droplets together using the other (the top) microscope slide. Similarly, a droplet could be placed on each slide to produce a horizontal interface.

Optical component positioning devices, translators, manufactured by the Oriel Corporation, were chosen for

moving the slides relative to each other because they have good precision and are available off-the-shelf. One X-Y translator and one vertical translator are used to give relative slide movement in three mutually orthogonal directions. Each of the positioning components works via one or two micrometers mounted between a moving platform and a stationary base. Their precision is good, with a claimed resolution of 0.3 μm .

The basic configuration of the apparatus consists of two large aluminium plates which are attached to opposite ends of the vertical translator. Each plate holds a microscope slide via a slide stage and the separation between the plates is controlled by the vertical translator micrometer. The top plate is a bracket which connects the vertical translator to the X-Y translator. The bottom plate is the base of the apparatus which bolts to a bracket on the optical microscope in place of the standard slide stage.

A schematic of the experimental configuration is illustrated in Figure 1a. This Figure displays the interconnections among the components of the apparatus. The major axes of the microscope slides are orthogonal so that the clips used to mount the slides do not limit the minimum gap between the slides. In this Figure the base (A) is shown holding the bottom slide stage (B), which holds the bottom microscope slide (C). The bottom slide stage is attached to the base with three bolts, and it can be easily removed from the apparatus to change the bottom microscope slide and to add the

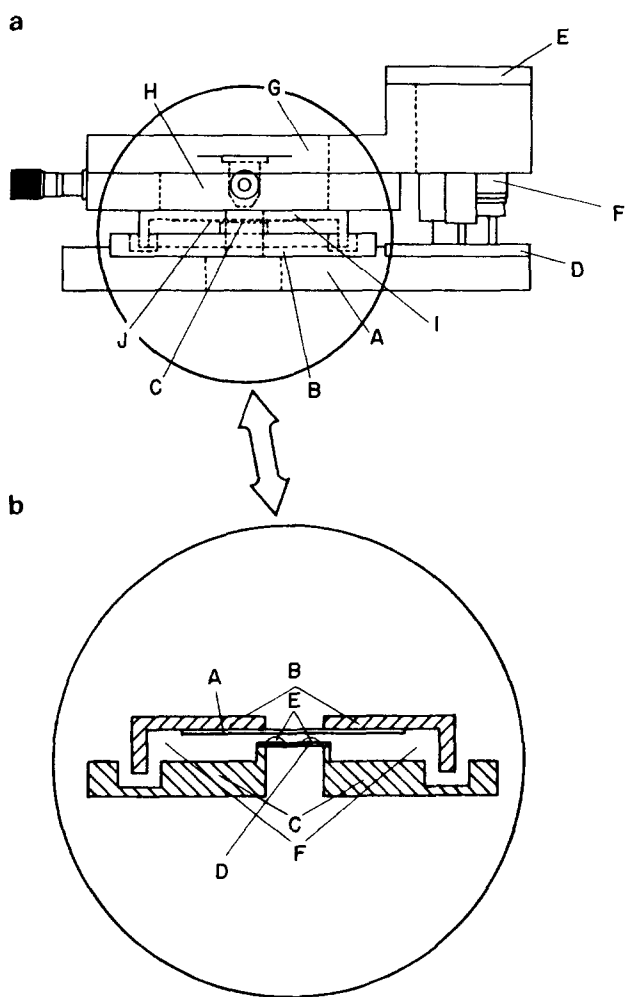


Figure 1 (a) Schematic of the interfacial microstage reactor; (b) cross section of reaction zone (see text for key)

monomer droplets to the apparatus. The bottom platform of the vertical translator (D) is also bolted to the base of the apparatus. The top platform of the vertical translator (E) moves relative to the bottom platform (D) via the micrometer (F) and holds the bracket (G). The stationary platform of the X-Y translator (H) is bolted to the bracket, and the moving platform holds the top slide stage (I). The top microscope slide (J) is mounted on the top slide stage using spring-loaded clips. All components other than the translators were machined from aluminium blocks.

In order to accommodate temperature control of the slides, an open-bottomed box is mounted on the top slide stage, and the bottom edge of this box fits into a groove in the bottom slide stage. A cross section of this part of the apparatus is shown in *Figure 1b*. This Figure displays the top microscope slide (A), the top slide stage (B), the bottom slide stage (C), the bottom microscope slide (D), and the monomer droplets (E). This configuration yields a control chamber (F) which is heated by cartridge heaters mounted on both slide stages and hot air which is blown over the exterior surfaces of the slides. Two cartridge heaters are used to heat each slide stage, and variable voltage power supplies are used to control the heaters. Air is heated by an air heater and directed over the exterior surfaces of the slides by nozzles. The temperature of the air is controlled by a temperature controller connected to a thermocouple.

The apparatus is shown in *Figure 2* mounted on a Zeiss optical microscope. Note the two large aluminium plates (the base and bracket) in this photograph. Also shown are the microscope light power supply, the 35 mm still camera and the temperature control system.

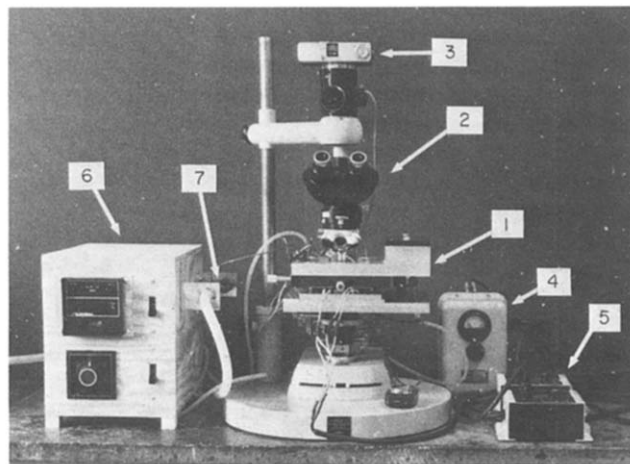


Figure 2 Interfacial microstage reactor on optical microscope: (1) interfacial microstage reactor; (2) optical microscope; (3) 35 mm still camera; (4) light power supply for microscope; (5) power supplies for cartridge heaters; (6) temperature controller for air heater; (7) air heater

The crosslinking system used consists of a trifunctional polyol (TONE 0305, Union Carbide) (triol) and a diisocyanate (143-L, Upjohn). The polyol is a polycaprolactone with a molecular weight of 540 g/mol. The diisocyanate is a liquid form (at room temperature) of diphenylmethane diisocyanate (MDI) with an isocyanate equivalent of 143.7 g/mol NCO. The catalyst used was dibutyltin dilaurate (CAT). The polyol was degassed before use and the diisocyanate was used as received. The triol/MDI system forms a crosslinked amorphous polymer; bulk adiabatic temperature rise experiments^{4c} yield a tough, transparent material. Since the trifunctional polyol has a relatively low molecular weight, giving short segments between crosslinks, the resultant polymer cannot readily crystallize.

The linear system used consists of two diols and a diisocyanate. The diols are 1,4 butanediol (BDO) for the chain extender and polypropylene oxide endcapped with polyethylene oxide (NIAX 12-56, Union Carbide) (PPO) for the long chain flexible diol. A liquid form of MDI (143-L, Upjohn) was also used in these experiments. Dibutyltin dilaurate catalyst (CAT) was mixed with the diol phase in some experiments. Studies were done with each of the diols separately, as well as with a mixture of them. The diols were degassed before use, and the diisocyanate was used as received. The BDO/PPO/MDI system is typical of a commercial urethane RIM system, and it produces a block copolymer containing hard and soft segments. The hard and soft segments are formed by the reactions between the diisocyanate (MDI) and the chain extender (BDO) and the diisocyanate (MDI) and the long chain diol (PPO), respectively. Concurrent with the polymerization are phase separation of the hard and soft segments into domains and crystallization of the hard segments into spherulitic structures.

The contact angle of each monomer with the glass slides was measured at 25°C using a model 100-00115 goniometer manufactured by Rame-Hart, Inc. Advancing and receding contact angles were measured; both angles were 44°, 53° and 38° for MDI, triol and BDO, respectively. The contact angles for PPO were: 35° advancing and 10° receding. All the contact angles are smaller than 90°, indicating that all the monomers wet the glass slides. Thus, when the monomers are contacted

EXPERIMENTAL PROCEDURE

The steps required to perform an experiment are as follows:

- (1) Prepare the monomers by mixing and degassing.
- (2) Raise the top slide stage using the vertical translator micrometer.
- (3) Remove the bolts and withdraw the bottom slide stage.
- (4) Install microscope slides on the top and bottom slide stages.
- (5) Place 0.01 ml droplets of the monomers on the bottom slide approximately 5 mm apart using micropipets.
- (6) Replace the bottom slide stage.
- (7) Allow the system to equilibrate thermally, if operating at elevated temperatures.
- (8) Lower the top slide stage until the top microscope slide touches both monomer droplets independently.
- (9) Focus the microscope.
- (10) Slowly lower the top slide stage until the drops contact and the experiment begins.
- (11) Record the experiment using the 35 mm camera, video recording or by means of visual observations.

CHEMICAL SYSTEMS

The monomers and catalyst used in these studies are commercially available materials intended for polyurethane RIM formulations. Both crosslinking and linear systems were used.

using the apparatus, they touch initially at their contact lines on the glass slides.

EXPERIMENTAL RESULTS

The experiments were performed at $T = 25^{\circ}\text{C}$ and at 70°C . Several runs were performed under each set of conditions to ensure reproducibility. Typical spacings between the microscope slides ranged from 100 to $500\ \mu\text{m}$. Small spacings were employed for experiments aimed at observing the polymer layer forming; large spacings were used for experiments intended for visualization of instabilities. The former minimized projection problems, while the latter decreased the constraints on motion in the neighbourhood of the interface.

Triol/MDI system

Several experiments were performed using the crosslinking system described above. The initial interface was somewhat difficult to form such that it was stationary and planar. In many cases, waves and fingers formed which contorted the interface enough that it was impossible to see an unambiguous projection of the interface. At high temperatures (70°C) the triol phase often moved into the diisocyanate phase, producing a highly contorted interface. With patience, though, and by

doing many runs, good initial conditions could be found. One such run at ambient conditions is shown in *Figure 3a*. In this micrograph the top phase is the triol (containing 0.1 wt% dibutyltin dilaurate catalyst) and the bottom phase is the diisocyanate. The polymer was difficult to locate throughout this experiment because it is transparent; bulk adiabatic temperature rise experiments^{4c} confirm this. After 25 min (*Figure 3b*) there were no substantial changes, but small spherical regions of polymer began to form on the diisocyanate side of the interface. These were difficult to spot initially, but became more distinct at longer times. The rippled structure in the neighbourhood of the interface is a transparent polymer film. This was verified by shearing the glass slides, which stretched and finally ruptured the film. At one hour, the region surrounding the interface appears as shown in *Figure 3c*. The system has essentially stopped evolving, and will appear no different at a much later time. At this point, the polymer is well defined only on the diisocyanate side of the interface. There is no evidence of polymer formation on the triol side of the interface, which may be due to an amorphous network structure being formed there.

If this system is examined under cross-polarized light at long times, a birefringent structure characteristic of spherulites is apparent (*Figure 3d*). This is somewhat

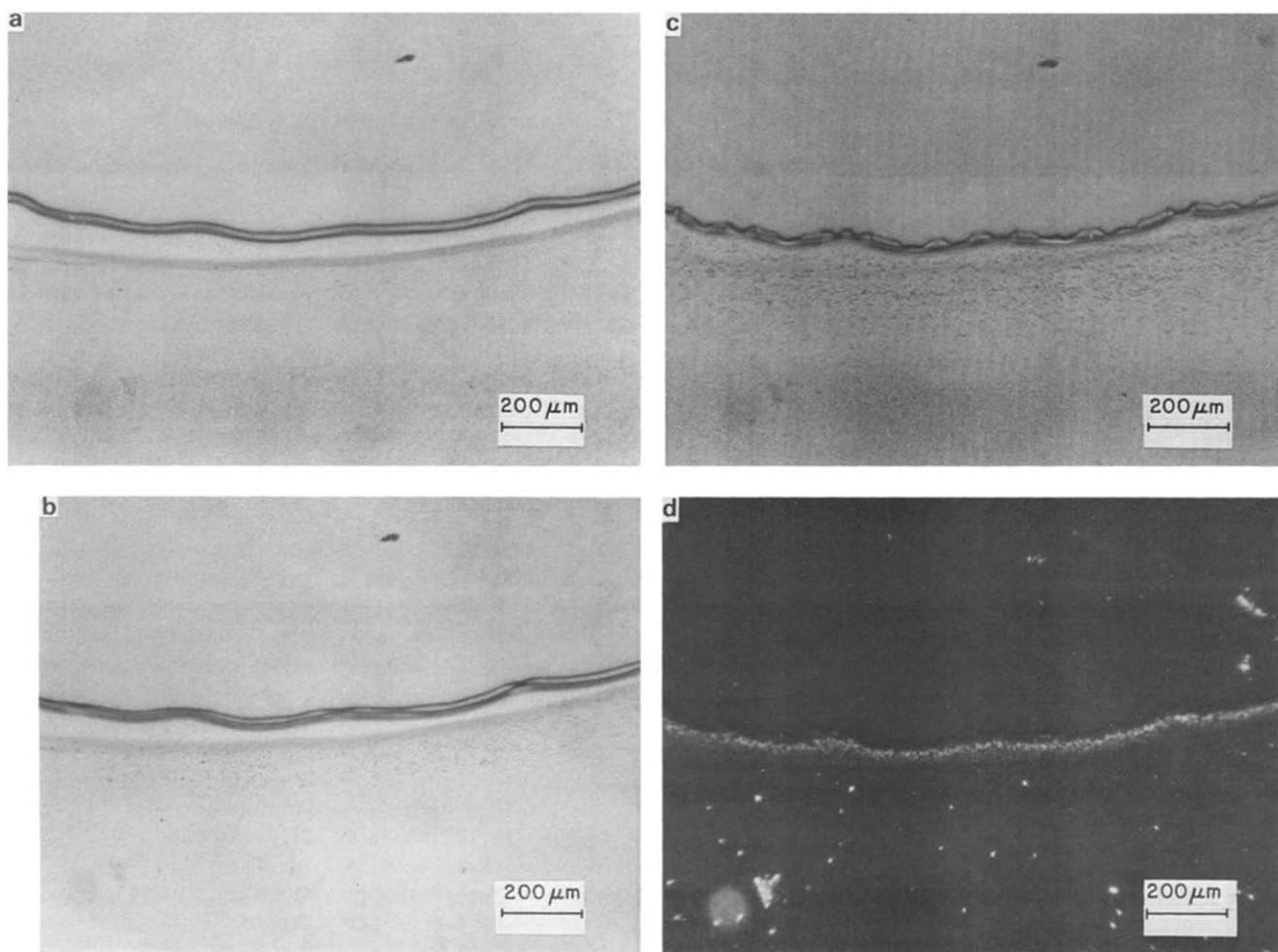


Figure 3 Interfacial polymerization at 25°C : top phase, triol + 0.1 wt% catalyst; bottom phase, diisocyanate. Time: (a) 0 s; (b) 25 min; (c) 1 h; (d) 1 h (crossed polarizers)

surprising, and is not expected for a crosslinking system. We believe that these spherulitic structures are not characteristic of the crosslinking system, but are instead due to a side reaction or other anomalous effect (see below). Some of the birefringence in the neighbourhood of the original interface is due to molecular orientation in the transparent polymer film. This can be induced by stretching the film by shearing the microscope slides.

To characterize the crystalline structure seen in this experiment, another experiment was carried out. A sample which had been polymerized at room temperature between a microscope slide and a cover glass was placed in a Mettler FP2 hotstage to try to measure the melting point of the spherulites seen in the diisocyanate phase. The sample was tested by increasing the temperature from room temperature at a rate of $10^{\circ}\text{C}/\text{min}$. Between 85°C and 120°C the spherulites disappeared; the birefringent band remained in the neighbourhood of the original interface. This band remained essentially unchanged up to 230°C , where the experiment was abandoned because the sample started degrading. Since the spherulites disappeared at relatively low temperatures, one can conclude that they were formed from some material other than the crosslinked polymer. The birefringent band which remained at high temperatures appears to be due to molecular orientation induced by stretching of the polymer film during the polymerization.

High temperature experiments gave similar results to the ones described above. At 70°C , the crosslinked film formed at the interface shut down the polymerization before domains were formed in either phase. After 10 min the system stopped changing, and is shown in *Figure 4a*. A corresponding photograph taken using crossed polarizers is shown in *Figure 4b*. Note that the film clearly shows birefringence in this case, but few polymer regions can be detected in either monomer phase.

BDO/MDI system

The interfacial polymerization between BDO and MDI was also studied. The initial conditions (just after the drops touched) was a stable, stationary, nearly planar interface between the monomer phases (see *Figure 5a*). In this photograph, the top phase is BDO with 0.1 wt% catalyst and the bottom phase is MDI. If uncatalysed and at room temperature, the polymerization was very slow, and it took several hours for the polymer to form in the vicinity of the interface.

The first discernible features which appeared were translucent spherical regions of hard segment polymer which formed on the BDO side of the interface. These regions appeared first near the interface and eventually formed up to $100\ \mu\text{m}$ from the interface (see *Figures 5b* and *5c*). This penetration distance is consistent with diffusion coefficients of the order $10^{-7}\ \text{cm}^2\ \text{s}^{-1}$. The concentration of these regions was maximum at the interface and decayed with increased distance from the interface. Under cross-polarized light (*Figure 5d*) these regions show little or no birefringence, and are concluded to be non-crystalline. We believe they are phase separated domains of hard segment polymer due to an incompatibility between the polymer and the BDO monomer.

During the polymerization, a diffuse band of polymer appears in the diisocyanate phase (*Figure 5c*). Under cross-polarized light (*Figure 5d*) this region is highly

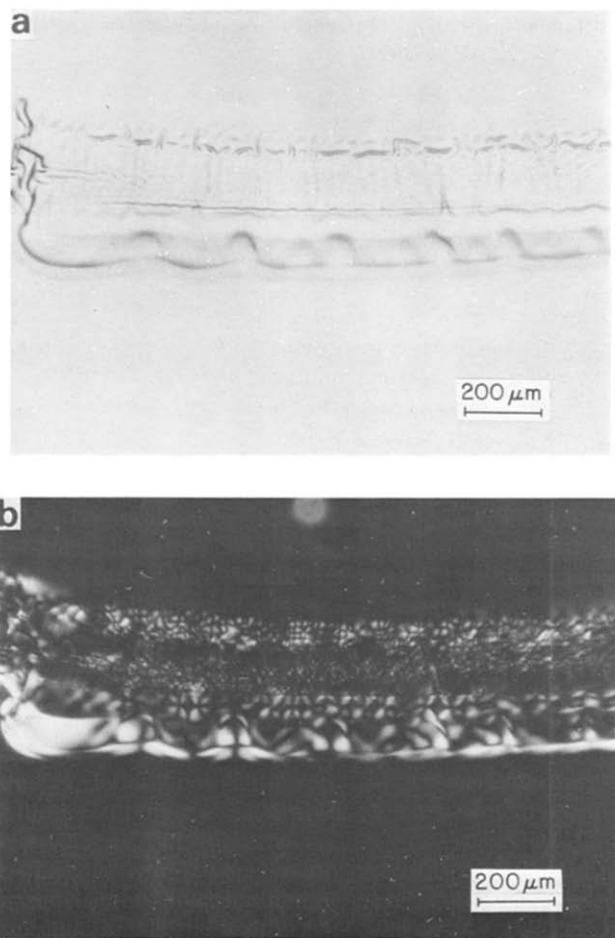


Figure 4 Interfacial polymerization at 70°C : top phase, triol + 0.1 wt% catalyst; bottom phase, diisocyanate. Time: (a) 10 min; (b) 10 min (crossed polarizers)

birefringent, and contains crystallites. The hard segment polymer appears soluble in MDI up to a particular molecular weight or concentration, at which point it crystallizes from the MDI-polymer solution.

The qualitative picture in the neighbourhood of the interface remains unchanged if the catalyst is not introduced into this system. Instead, both types of domain formation occur over a longer time.

Experiments performed at high temperatures (70°C) gave the same behaviour, although the process was faster and the domains formed within several minutes.

PPO/MDI system

A stable, stationary interface could not be formed between PPO and MDI. When the droplets were contacted, an interface was initially formed, but it disappeared within the first 30 s of the experiment; the interface smeared due to the spontaneous generation of interfacial area. After several minutes no trace of the initial interface could be located. This may be explained with a different experiment. A small droplet of one of the monomers was placed in a much larger pool of the other monomer. When the diisocyanate was placed in the diol, the droplet remained intact, but its surface did not remain quiescent. Interfacial area was generated, contorting the interface. Layers of the reactants were wrapped up at the

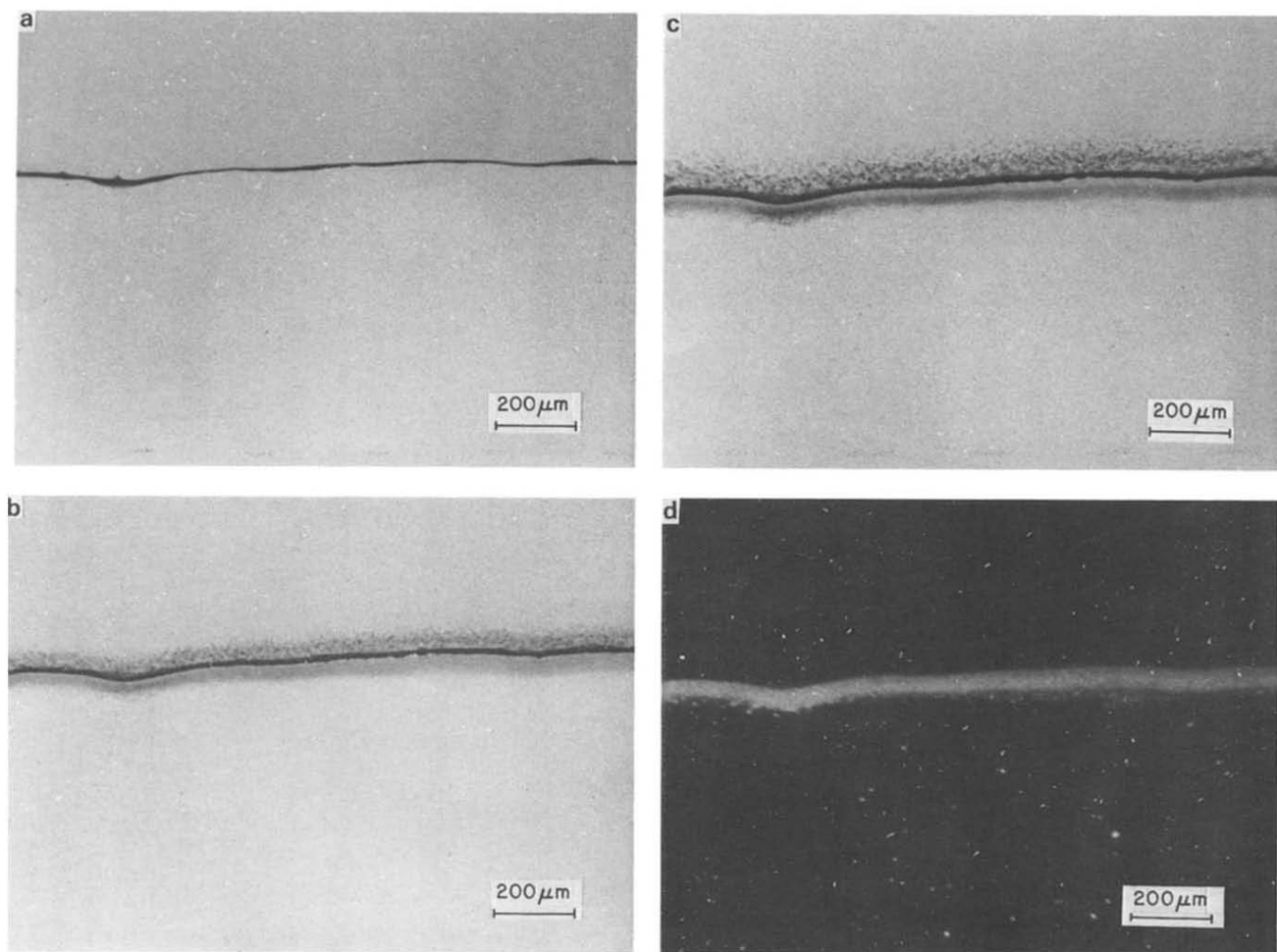


Figure 5 Interfacial polymerization at 25°C: top phase, BDO + 0.1 wt % catalyst; bottom phase, diisocyanate. Time: (a) 0s; (b) 10 min; (c) 20 min; (d) 20 min (crossed polarizers)

edge of the MDI droplet. In contrast, when the long chain diol was placed in the diisocyanate, the PPO droplet spread into a thin layer, covering the entire MDI pool. From these observations, it is apparent that when the two monomers are contacted, interfacial area is generated continuously until the monomers are mixed. Since the polymer formed is amorphous and translucent, it could not be located in the experiments.

BDO/PPO/MDI system

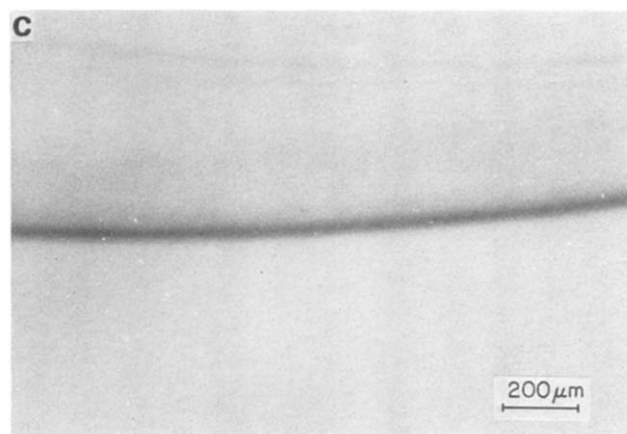
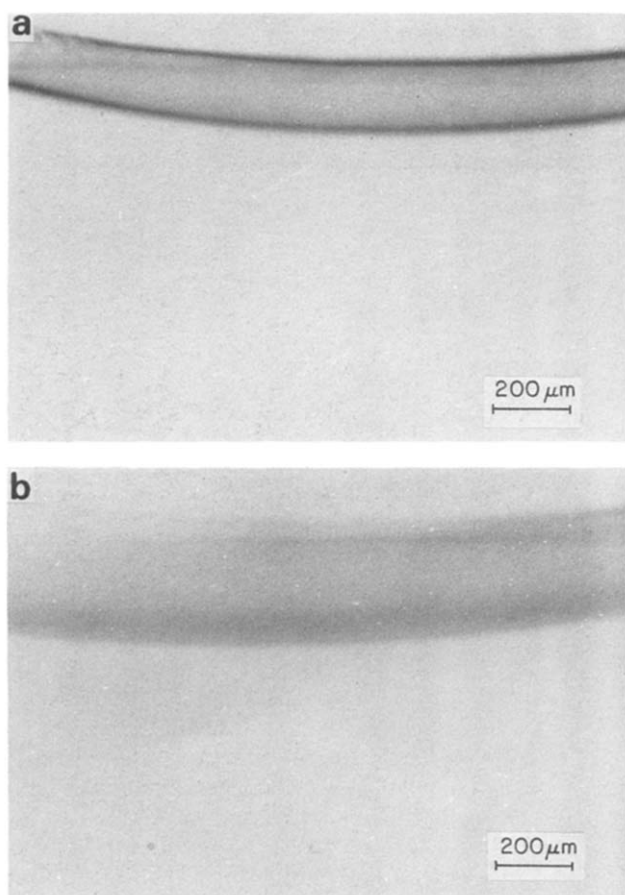
The three component system was also studied by contacting a mixture of BDO and PPO with MDI. Three diol mixtures were examined: 25%, 50% and 75% BDO by weight (see Table 1). In all the experiments the interface formed was not stable; a stationary, planar interface could not be formed. The character of the instability was dependent on the composition of the diol phase and the temperature. When the 25% BDO mixture was contacted at room temperature with MDI, the diols moved into the diisocyanate phase, smearing the interface. A sequence of photographs which depicts this is shown in Figures 6a-c. In contrast, when a 50% mixture was used, the system often formed a set of roll cells which wrapped up the interface. This is shown in Figures 7a-d. Each cell contains two counter-rotating vortices. Sometimes cells

were not produced for this system; instead, more complex motion occurred in the neighbourhood of the interface. The 75% BDO mixture produced 'twitching' (rapid sporadic movements along the interface, but little flow perpendicular to the interface) of the interface, with some small scale mixing in the neighbourhood of the interface (Figure 8).

Another method of testing the stability of the interfaces formed by this system is to place one monomer droplet on each microscope slide and contact them so that a large horizontal interface is produced between the droplets; this type of interface is less constrained by the microscope slides. The microscope can then be focused on the interfacial plane, allowing the observation of the interfacial motion from an orthogonal viewpoint compared to the other experiments. When the 25% BDO system is contacted this way, no instability can be detected. In fact, it is difficult to focus the optical microscope on the interface. In contrast, the 50% mixture shows vigorous motion at the interface, and cells can be seen (Figure 9). This photograph was taken at the same time during the experiment (30 s) as Figure 7c. Note that both these photographs show cells with the same characteristic size (200 μm). The 75% BDO system shows moderate motion in this experiment (Figure 10),

Table 1 Interfacial experiments: observations

Droplet 1	Droplet 2	T (°C)	Observations
<i>Crosslinking system:</i>			
Triol/CAT	MDI	25	Fingering
Triol/CAT	MDI	70	Fingering, triol phase penetrates diisocyanate
<i>Linear system:</i>			
BDO/CAT	MDI	25	Stable interface
BDO/CAT	MDI	70	Stable interface
PPO/CAT	MDI	25	Stable interface cannot be formed (smears)
PPO/CAT	MDI	70	Stable interface cannot be formed (smears)
BDO/PPO/CAT (25/75 by wt)	MDI	25	Diols penetrate diisocyanate, interface smears
BDO/PPO/CAT (25/75 by wt)	MDI	70	Diols penetrate diisocyanate, interface smears
BDO/PPO/CAT (50/50 by wt)	MDI	25	Instabilities: roll cells
BDO/PPO/CAT (50/50 by wt)	MDI	70	Instabilities: no roll cells
BDO/PPO/CAT (75/25 by wt)	MDI	25	Instabilities: twitching interface
BDO/PPO/CAT (75/25 by wt)	MDI	70	Instabilities: twitching interface


Figure 6 Interfacial polymerization at 25°C: top phase, 25% BDO + 75% PPO + 0.1 wt% catalyst; bottom phase, diisocyanate. Time: (a) 30s; (b) 1 min; (c) 2 min

but less than was seen for the 50% BDO mixture. This is consistent with the results of the previous experiment (Figure 8).

Somewhat surprisingly, the high temperature experiments show less active interfacial instabilities than those at room temperature. The 50% BDO system again shows the largest amount of motion at the interface, but roll cells are no longer present. The higher temperature may suppress the instabilities because the interfacial tension might decrease; interfacial tensions typically decrease with increasing temperature.

The three component system exhibits layering of the polymer products in all experiments. Recent computer simulations^{4a,b} indicate similar results. The polymer formed for the 25% BDO and the 50% BDO mixtures at room temperature is shown in Figures 11a and 12a. The

corresponding cross-polarized photographs are displayed in Figures 11b and 12b. Note that both sets of photographs show complex structures due to the motion in the neighbourhood of the interface during polymer formation. In all cases, a layer of birefringent hard segment-rich material is formed on the diisocyanate side of the interface. This is presumably due to the diffusion of BDO into the MDI, and this observation is consistent with the arguments of Chang *et al.*³, Kolodziej *et al.*¹ and Chen *et al.*² concerning the production of layered structures due to mixing effects. High temperature experiments (70°C) yield the same type of structure (Figure 13a and 13b), but the effects of interfacial instabilities are less important, as mentioned above. By continuing to squeeze the droplets during the first thirty seconds of the experiments, the interface could be stabilized at high temperatures. This gave runs which could be used to examine the layered structure with more confidence. Figures 13a and 13b are for a 25% BDO system. Both 50% BDO and 75% BDO systems gave comparable results. Note that there is again a layer of crystalline hard segment material on the diisocyanate side of the interface. The polymer produced on the diol side of the interface is non-crystalline; this is probably due to the large fraction of soft segment in the polymer chains.

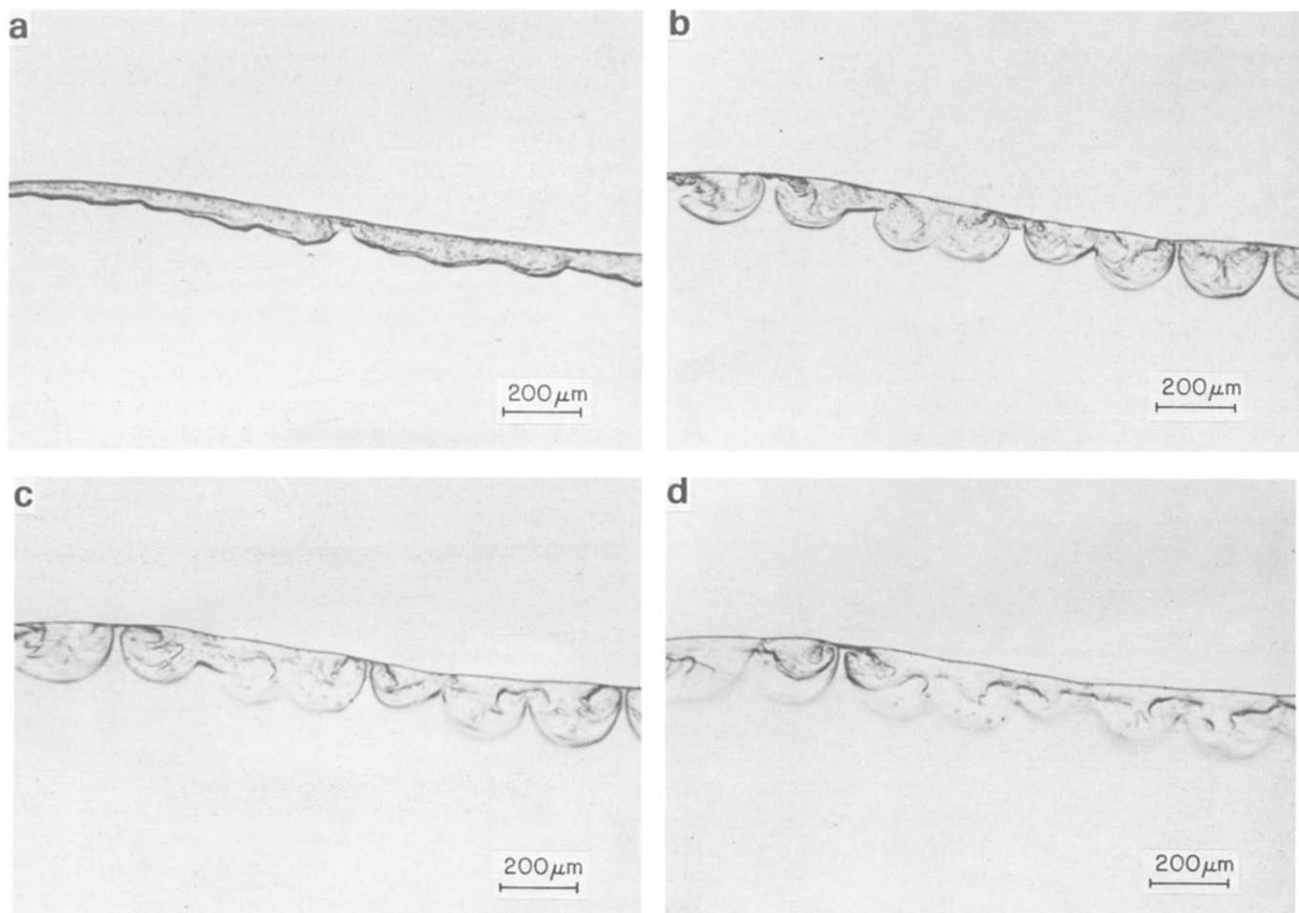


Figure 7 Interfacial polymerization at 25°C: top phase, 50% BDO + 50% PPO; bottom phase, diisocyanate. Time: (a) 10s; (b) 20s; (c) 30s; (d) 60s

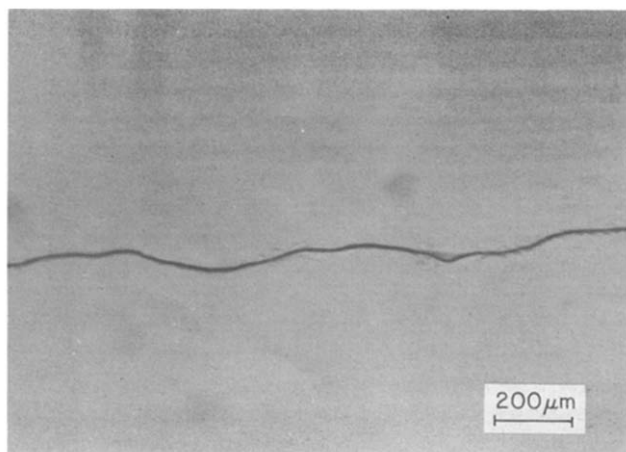


Figure 8 Interfacial polymerization at 25°C: top phase, 75% BDO + 25% PPO + 0.1 wt% catalyst; bottom phase, diisocyanate. Time: 15s

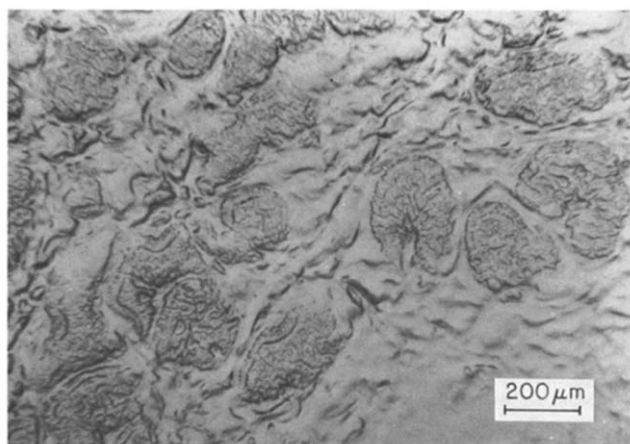


Figure 9 Interfacial polymerization at 25°C (alternative method): top phase, 50% BDO + 50% PPO; bottom phase, diisocyanate. Time: 30s

Photographs of another experiment at higher magnification show the typical spherulitic superstructure of the crystalline regions (Figures 14a and 14b).

CONCLUSIONS

We have demonstrated the application of a new apparatus to the observation of interfacial polymeri-

zations. Its main advantage is that it provides good control in forming the interface. Experiments were conducted for both linear and crosslinking urethane systems. We encountered several expected and several unexpected phenomena occurring during interfacial polymerizations which have practical importance and are relevant to previous morphological studies. Table 1 summarizes the effects noted in the experiments. The

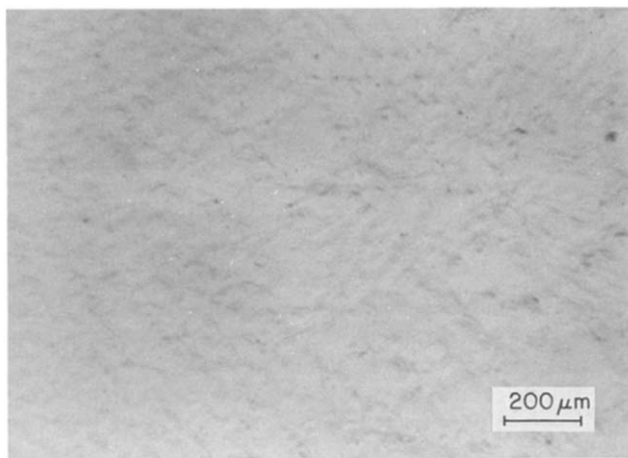


Figure 10 Interfacial polymerization at 25°C (alternative method): top phase, 75% BDO + 25% PPO + 0.1 wt% catalyst; bottom phase, diisocyanate. Time: 10s

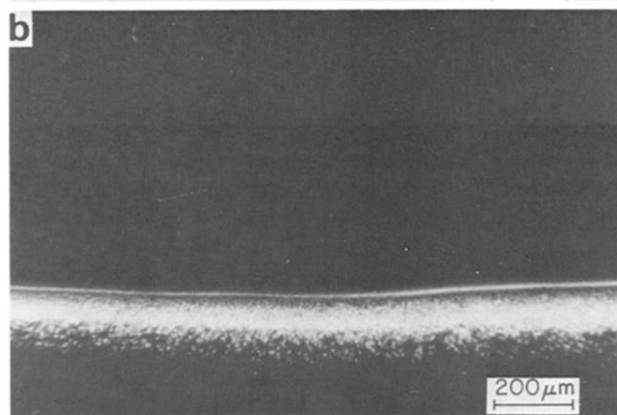
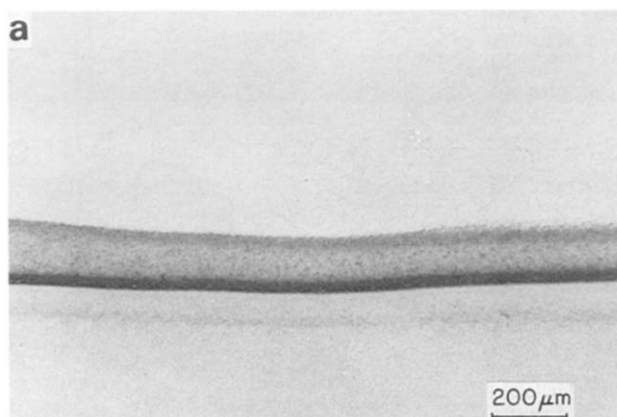


Figure 12 Interfacial polymerization at 25°C: top phase, 50% BDO + 50% PPO + 0.1 wt% catalyst; bottom phase, diisocyanate. Time: (a) 1 h; (b) 1 h (crossed polarizers)

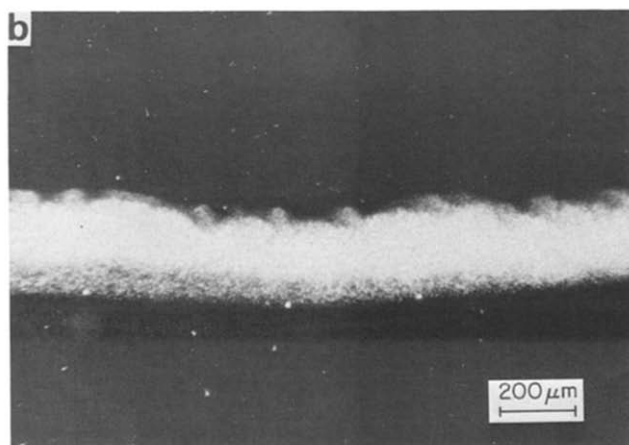
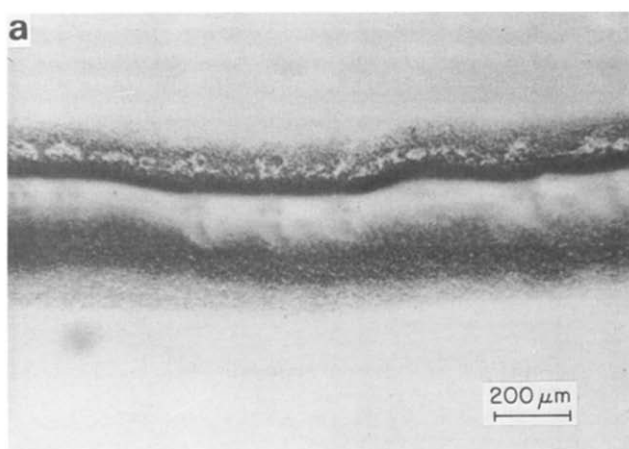


Figure 11 Interfacial polymerization at 25°C: top phase, 25% BDO + 75% PPO; bottom phase, diisocyanate. Time: (a) 2.5 h; (b) 2.5 h (crossed polarizers)

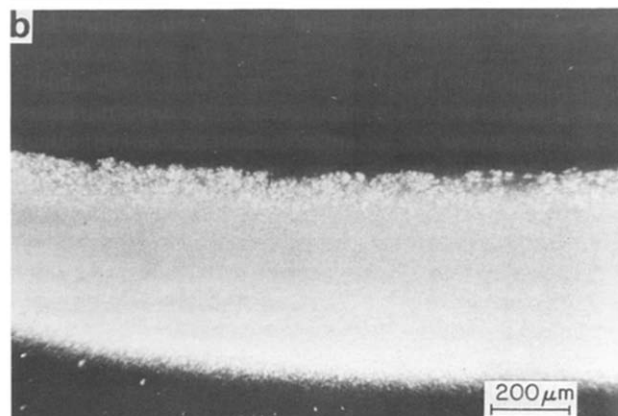
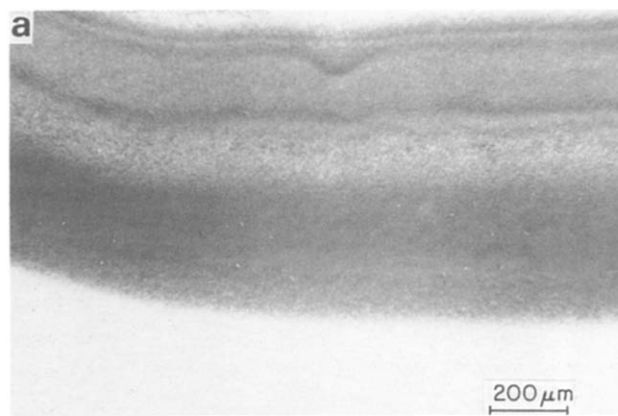


Figure 13 (a) Interfacial polymerization: top phase, 25% BDO + 75% PPO + 0.1 wt% catalyst; bottom phase, diisocyanate. Time: 10 min; temperature: 70°C. (b) Interfacial polymerization: top phase, 25% BDO + 75% PPO + 0.1 wt% catalyst; bottom phase, diisocyanate. Time: 10 min; temperature: 70°C (crossed polarizers)

interface may or may not be stable, and spontaneous mixing of the monomers may occur in the neighbourhood of the interface. However, the spontaneous mixing occurs only for the three component system, and it is not dependent on catalyst location. This led us to believe that it is a marangoni-type instability²², and that gradients in the interfacial tension arise from gradients in the composition along the interface. Since a three component system is required to produce gradients in composition

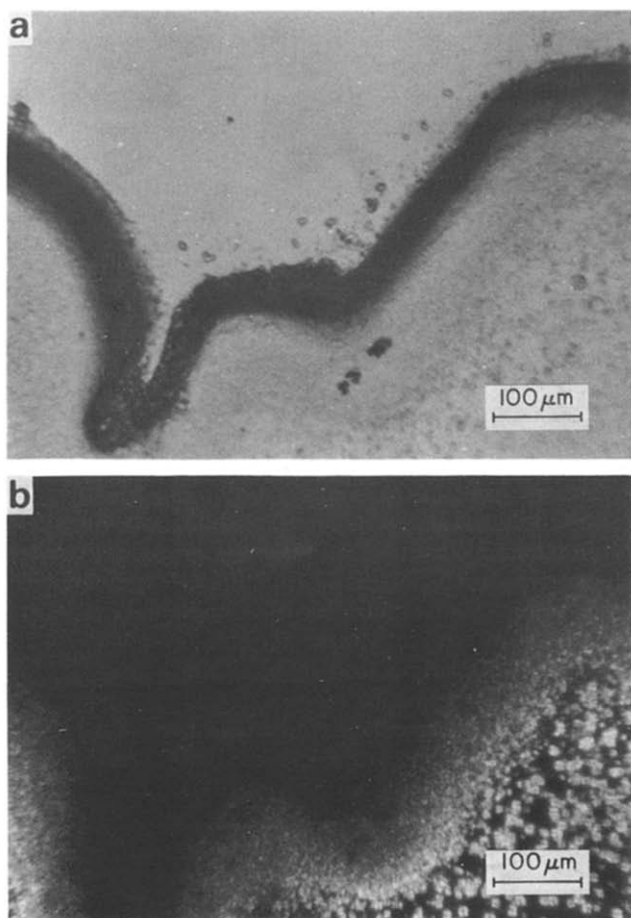


Figure 14 Interfacial polymerization at 70°C: top phase, 75% BDO + 25% PPO + 0.1 wt% catalyst; bottom phase, diisocyanate. Time: (a) 30 min; (b) 30 min (crossed polarizers)

along an interface, this is a plausible explanation. This spontaneous mixing occurs at length scales (100 μm) and time scales (10–30 s) as to be of practical importance, for example, in RIM. One may want to promote it to supplement mechanical mixing, since stretching of the interface enhances the reaction rate (for a theoretical study, see ref. 4b).

Fingering of the interface occurs in many cases, as does one monomer penetrating the other. The fluid mechanics in the neighbourhood of the interface is complex, and it is intimately related to the diffusion–reaction process occurring there. At the moment the modelling of such a problem appears exceedingly complicated, especially when one considers the many unanswered questions that arise during the fingering of fluids^{2,3}.

Product (hard/soft segment) segregation has been seen in previous morphological studies^{2,3,24} and imperfect

mixing has been used as an explanation. The experiments presented here reinforce these ideas, since hard and soft segment layers are formed in the neighbourhood of the interface due to diffusional effects. Theoretical computations^{4a,b} agree qualitatively with these observations.

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