TRANSIENT INTERFACIAL PHENOMENA IN MISCIBLE POLYMER SYSTEMS (TIPMPS)

John A. Pojman[1*], Nicholas Bessonov[2], Vitaly Volpert[2] and Hermann Wilke[2]

University of Southern Mississippi[1], Université Lyon I[2] and Institute of Crystal Growth, Berlin[2]

Almost one hundred years ago Korteweg published a theory of how stresses could be induced in miscible fluids by concentration gradients, causing phenomena that would appear to be the same as with immiscible fluids. Miscible fluids could manifest a "transient" or "effective" interfacial tension (EIT). To this day, there has been no definitive experiment to confirm Korteweg's model but numerous fascinating and suggestive experiments have been reported. The goal of TIPMPS is to answer the question: *Can concentration and temperature gradients in miscible materials induce stresses that cause convection?*

Many polymer processes involving miscible monomer and polymer systems could be affected by fluid flow and so this work could help understand miscible polymer processing, not only in microgravity, but also on earth. Demonstrating the existence of this phenomenon in miscible fluids will open up a new area of study for materials science. As the TIPMPS SCR Panel, December 2000 stated:

"If gradients of composition and temperature in miscible polymer/monomer systems create stresses that cause convection then it would strongly suggest that stress-induced flows could occur in many applications with miscible materials. The results of this investigation could then have potential implications in polymer blending (phase separation), colloidal formation, fiber spinning, polymerization kinetics, membrane formation and polymer processing in space."

The science objectives of TIPMPS are:
1) Determine if convection can be induced by variation of the width of a miscible interface
2) Determine if convection can be induced by variation of temperature along a miscible interface
3) Determine if convection can be induced by variation of conversion along a miscible interface

An interface between two miscible fluids can best be created via a spatially-selective photopolymerization of dodecyl acrylate with a photoinitiator, which allows the creation of precise and accurate concentration gradients between polymer and monomer (Figure 1). Optical techniques will be used to measure the refractive index variation caused by the resultant temperature and concentration fields. The viscosity of the polymer will be measured from the increase in the fluorescence of pyrene

Because the large concentration and temperature gradients cause buoyancy-driven convection that prevents the observation of the predicted flows, the experiment must be done in microgravity.

In this report, we will consider our efforts to estimate the square gradient parameter, k, and our use of the estimates in modeling of the planned TIPMPS experiments. We developed a model consisting of the heat and diffusion equations with convective terms and of the Navier-Stokes equations with an additional

volume force written in the form of the Korteweg stresses arising from nonlocal interaction in the fluid. The fluid's viscosity dependence on polymer conversion and temperature was taken from measurements of poly(dodecyl acrylate). Numerical modeling demonstrated that significant flows would arise for conditions corresponding to the planned experiments.
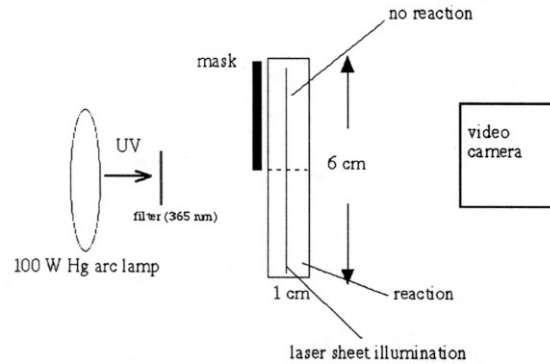

Figure 1. A schematic of the TIPMPS experiment in which UV light and a mask are used to create gradients between dodecyl acrylate and its miscible polymer.

Background
Korteweg proposed in 1904 that a nonuniform concentration distribution leads to stresses in a fluid. [1] Anderson and McFadden modeled internal waves in a near-critical fluid using a Korteweg stress term in the momentum equation.[2] Joseph and Renardy considered many aspects of Korteweg stresses in miscible fluids.[3]

A single fluid at equilibrium has a free energy that is constant throughout the volume. The free energy of a nonuniform fluid can be treated by including a term proportional to the square of the concentration gradient. The expression for the free energy at a location is now a functional because it depends on the concentration beyond the location. Cahn and Hilliard developed the theory based on what is often called the Ginzburg-Landau free energy functional, in 1958.[4]

In an earlier work,[5] we reviewed the work on effective interfacial tension, Korteweg stress and miscible fluids. For systems far from equilibrium, the composition can be nonuniform even if the liquids are miscible. We can write the free energy functional as

$$F = \int_\Omega f_0 dx + \sigma A \tag{1}$$

where

$$\sigma = k \int_\Omega |\nabla c|^2 d\xi \tag{2}$$

is the effective interfacial tension, and A the area of the interface.

If we consider a linear concentration gradient in one dimension, we can write:

$$\sigma = k \frac{\Delta c^2}{\delta} \tag{3}$$

where δ is the length over which the concentration changes, and Δc is the difference in composition, expressed in mole fraction, (Figure 2).

Zeldovich analyzed the problem of a miscible "interface" in 1949 and concluded that indeed a transient interfacial tension would exist.[6]
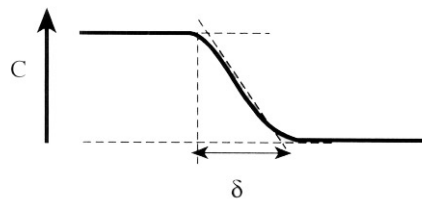

Figure 2. A schematic of an interface between miscible fluids.

Rousar and Nauman demonstrated that assuming a linear concentration gradient the surface tension can be found **without** assuming the system is at equilibrium.[7] They demonstrated analytically that across a linear concentration gradient, there is a difference between the pressure normal to the "interface" and pressure tangential to it:

$$p_N - p_T = k\left(\frac{dc}{dx}\right)^2 \tag{4}$$

If we integrate across the interface we calculate:

$$\sigma = \int k\left(\frac{dc}{dx}\right)^2 dx \tag{5}$$

Estimation of the Square Gradient Parameter
We estimate the value of k by using thermodynamic theory for polymer in a solvent and by spinning drop tensiometry. Balsara and Nauman derived a relationship:[8]

$$k = \frac{R_{gyr}^2 RT}{6V_{molar}}\left[X + \frac{3}{1-C}\right] \tag{6}$$

where R_{gyr} is the radius of gyration of the polymer, X is the Flory-Huggins interaction parameter. When multiplied by RT it provides the enthalpy of mixing between polymer and solvent. For a good solvent, it is 0.45. V_{molar} is the molar volume of the solvent, which in our case is the monomer, 2.7×10^{-4} m^3 mole^{-1}. We do not know R_{gyr} for poly(dodecyl acrylate) but we can obtain an upper estimate from literature results. For polystyrene in toluene at 60 ˚C, $R_g^2 = 9 \times 10^{-16}$ m^2. Because the concentration across the transition zone varies from 0 to 1, we average the expression up to C = 0.99 to obtain at 100 ˚C,

$$k = 5 \times 10^{-8} \text{ N}$$

The value of the radius of gyration was for high molecular polystyrene (10^6) but the polymer in TIPMPS will be lower. So if we assume an $R_g = 3 \times 10^{-9}$ m, k could be two orders of magnitude smaller.

It is important to note that this theory predicts that k increases with temperature.

Spinning Drop Tensiometry
The interfacial tension between two fluids can be measured using spinning drop tensiometry, which was developed by B. Vonnegut.[9] The principle is simple: The more dense fluid is placed into a capillary that is rotated at > 5,000 rpm (Figure 3). A drop of the less dense fluid is injected into the capillary. The drop is subject to a pressure jump across the interface, which stretches the drop along the axis of rotation. If this were the only force, the drop would extend until it reached the ends of the capillary and form a column of

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fluid inside the more dense phase. Because the volume of the drop is fixed, as the drop stretches, its area increases. Thus the free energy of the surface increases. The longer the drop and the smaller the radius, the lower is the rotational energy but necessarily the surface area is greater. Thus the equilibrium drop radius can be found by finding the minimum energy as a function of radius.
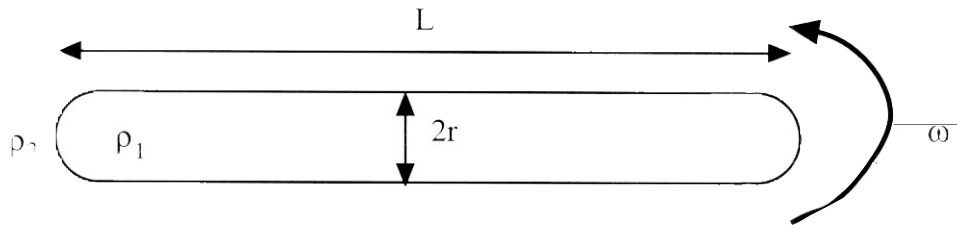

Figure 3. Schematic of a spinning drop

For L >> r, we have the simple relationship:

$$\sigma = \frac{\Delta \rho \omega^2 r^3}{4} \tag{7}$$

Petitjeans measured the EIT for glycerin/water and found that the drop diameter reached a quasi-steady value after 100 seconds.[10] He obtained a value at room temperature of 0.6 mN/m.

We studied dodecyl acrylate in poly(dodecyl acrylate), which we prepared by photopolymerization. We adjusted the molecular weight, and thus the viscosity, by adding dodecyl mercaptan, a chain transfer agent. We prepared it so the viscosity was about 0.1 Pa s at room temperature, the viscosity we will use at 100 ˚C in the flight experiment.

The densities of the polymer and monomer were measured with a Paar densitometer. A dye, zinc meso-tetraphenylporphine, was added to the monomer. A diode laser sheet was used to illuminate the drop, which was imaged orthogonally. Digital images were analyzed with NIH Image. The drop diameter was defined as the regions in which the spatial derivative of the gray scale was non-zero.
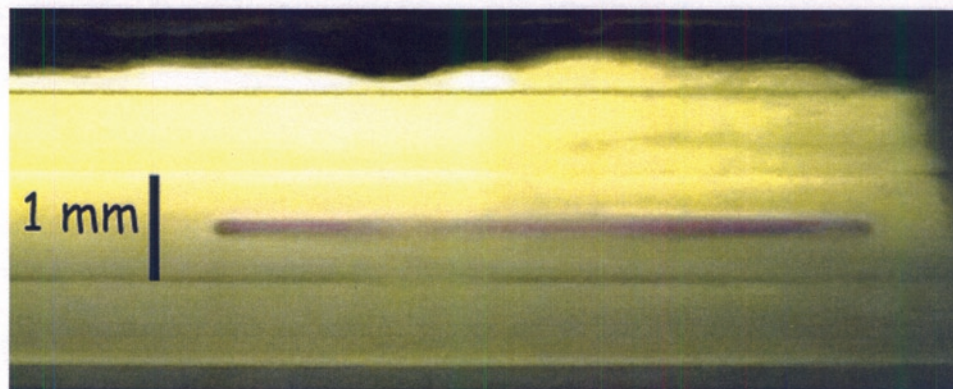

Figure 4. A drop of monomer with dye in poly(dodecyl acrylate) at 25 ˚C and a rotation rate of 5,000 rpm

Figure 4 shows a drop of monomer after it has mechanically relaxed, a process that requires about 100 seconds. Figure 5 shows that after the mechanical relaxation, the drop radius reaches a quasi-steady value. Hu and Joseph showed that the apparent interfacial tension for immiscible fluids increased with

rotation rate until reaching an asymptotitc value at rotoations exceeding 6,000 rpm.[11] We observed similar behavior for our miscible system with an asymptotic value of 0.08 mN/m for interfacial tension.

Note that in Figure 5 the interfacial tension appears to increase after 1000 s. In fact, it is the radius of the drop but not EIT that increases with time. This can happen if diffusion will have a greater impact on decreasing the density difference than on EIT. Thus, measurements with SDT of EIT in systems with large diffusion coefficients can be complicated because of this dual action of diffusion. The apparent faster rate of growth with time for higher rotation rates is an artifact of the ω^2 dependence of the interfacial tension. In fact, the radius grows at about the same rate for all drops.
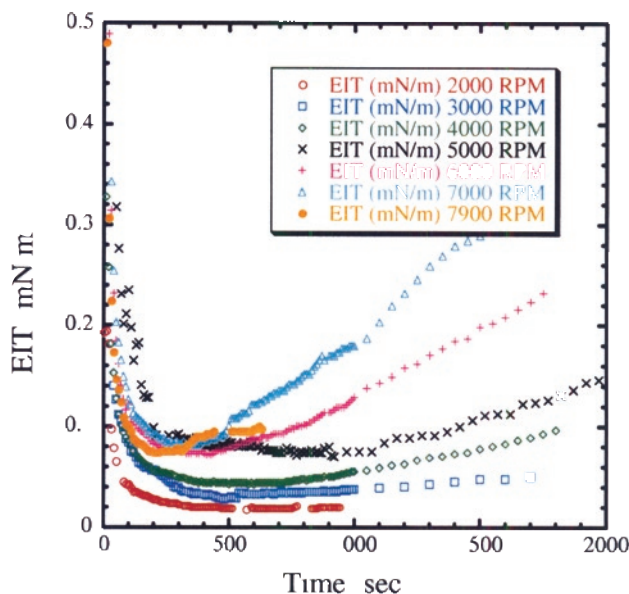

Figure 5. The dependence of the apparent effective interfacial tension on the rotation rate and time.

We estimated the width of the transition zone, δ, to be 10^{-4} m, which yields a value of k = 10^{-8} N. In a previous work,[5] we explained how we estimated the square gradient parameter from dodecyl acrylate/ poly(dodecyl acrylate) and for glycerin/water using spinning drop tensiometry.[5]

Numerical Modeling
We have developed a mathematical model for Korteweg stresses in miscible fluids in which the stress tensor terms are added to the incompressible Navier-Stokes equation. To study the influence of the effective interfacial tension on a monomer and its miscible polymer we consider mass, energy and momentum conservation. If we assume:
   a) Thermal and diffusive fluxes are small,
   b) The internal energy has the form,

$$e = e_0 + k|\nabla c|^2 \qquad (8)$$

   c) capillary forces are tangential to the composition gradient,
   d) the fluids are incompressible and have the same density and viscosity, we obtain the following model.

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$$\frac{\partial T}{\partial t} + v\nabla T = \kappa\Delta T$$

$$\frac{\partial c}{\partial t} + v\nabla c = D\Delta c$$

(9-12)

$$\frac{\partial v}{\partial t} + \left(v\nabla\right)v = -\frac{1}{\rho}\nabla p + v\Delta v + \frac{1}{\rho}\begin{cases}\dfrac{\partial K_{11}}{\partial x_1} + \dfrac{\partial K_{12}}{\partial x_2}\\[2mm]\dfrac{\partial K_{21}}{\partial x_1} + \dfrac{\partial K_{11}}{\partial x_2}\end{cases}$$

div v=0

Where T is the temperature, v is the fluid velocity, p is the pressure, v is the kinematic viscosity, ρ is the density and c is the concentration (mole fraction) of polymer. K_{ii} are the stress tensor terms, defined by:

$$K_{11} = k\left(\frac{\partial c}{\partial x_2}\right)^2$$

$$K_{12} = K_{21} = -k\frac{\partial c}{\partial x_1}\frac{\partial c}{\partial x_2}$$

(13-15)

$$K_{22} = k\left(\frac{\partial c}{\partial x_1}\right)^2$$

where k is system specific, with units of N.

Simulation of Three Cases

We previously validated the model by comparing steady-state simulations, in which the concentration field was fixed, to steady-state simulations of a true interface model.[5] We have demonstrated that drops of miscible fluids can spontaneously become spherical and that streams can exhibit a Rayleigh-like instability.[12] This model used a fixed grid, constant viscosity with the vorticity-stream function formulation.

We applied another numerical method with the conservation laws (mass, momentum, energy) in integral form (not in differential form) that allows us to introduce a viscosity that is dependent on the concentration.[13] Instead of the "stream-function and vorticity" we used "pressure-velocity" as the basic variables. We used nonorthogonal Eulerian or Lagrangian meshes. Figure 6 shows the simulation domain. The dependence for the viscosity on the conversion was taken as $v(c) = v_0 e^{\lambda c}$, with $\lambda = 3, 4$ or 5.
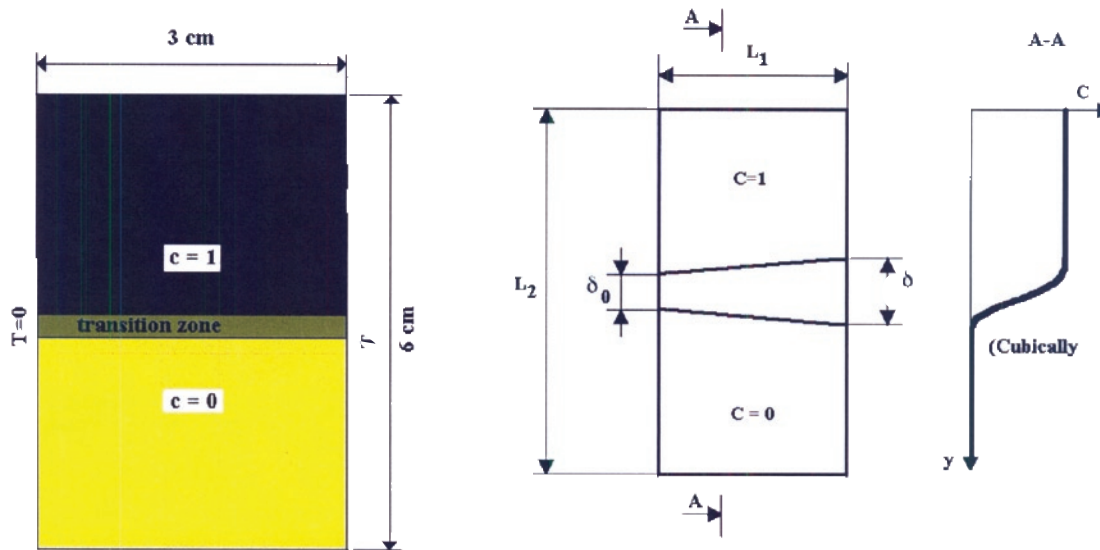
Figure 6. Left: Schematic of the simulation domain. Right: The configuration of the simulations with the variation in the width of the transition zone.
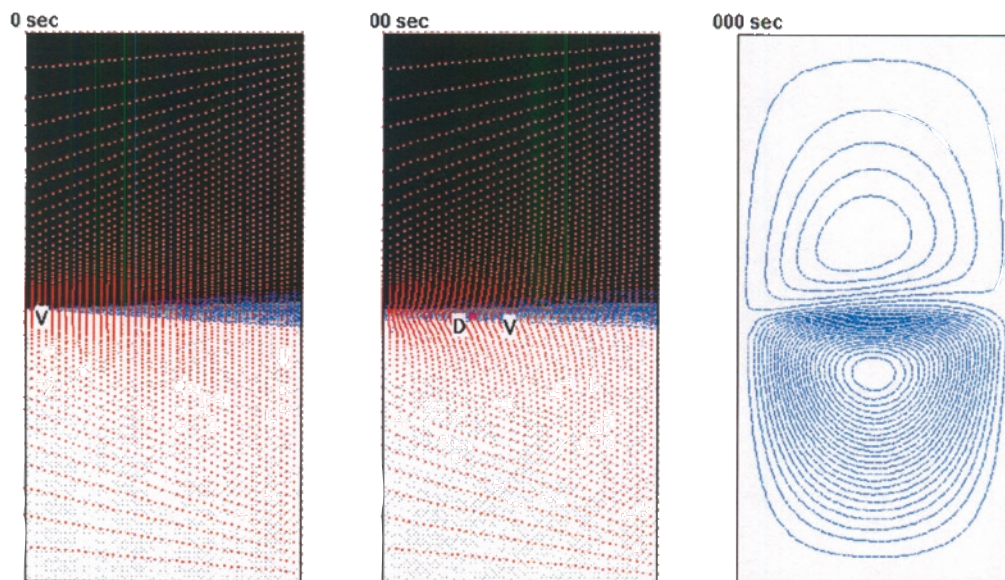
1. Variation in the transition zone.

Figure 7. Simulation with a variable transition zone: δ from 0.2 mm to 5 mm with k = 2 x 10^{-9} N. Polymer concentration is indicated by the gray level.

Figure 6 shows how the transition zone can either be constant or depend on position. If we impose an initial variation on the transition zone, significant flows can occur. Figure 7 shows the fluid displacement and the streamlines after 1000 seconds. Figure 8 demonstrates how the flow increases with the value of k and with the variation in δ but not indefinitely. A variation of 0.2 mm to 5 mm appears to be optimal.
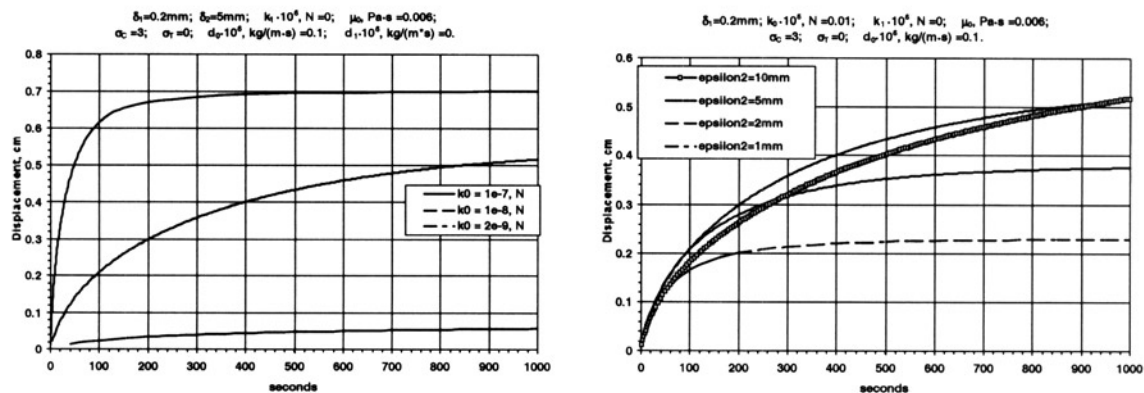
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Figure 8. Left: The maximum displacement of fluid as a function of time for different values of k. Right: The maximum displacement for different values of the transition width variance.

2. Effect of Temperature Gradients

We modeled a uniform concentration gradient (constant δ) with a linear temperature gradient parallel to the interface. We studied many cases but we discuss two here. First, we used eq. 6 to estimate the temperature-dependence of k. Figure 9 shows that with a 50 K temperature variation along the transition zone, the induced flow would be extremely weak. However, we estimate that such a change in T would increase the diffusion coefficient four times. When we include that effect with a k that is constant, a significant flow is induced (Figure 9). This occurs because the gradient in the diffusion coefficient creates a gradient in δ.

3. Variation of concentration

The final case is with a constant transition width, no applied temperature gradient but with a gradient in the polymer conversion. The polymer conversion and temperature are linked because complete conversion increases the temperature by 150 K. Figure 10 shows how a significant flow develops. If we include the temperature-dependence of D, then competing effects produce two flows. Although the total fluid displacement can be rather small, the distortion to the concentration field should be readily measurable using optical techniques.

Conclusions

We performed simulations based on Korteweg stresses using parameters for the TIPMPS flight investigation. Convection could be caused by temperature gradients or concentration gradients parallel to the large gradient between the miscible fluids. A variation in the width of this transition also caused convection.

Interesting effects occur if the diffusion coefficient is also temperature dependent.

Our next steps are to include the photopolymerization chemistry and to extend the model to three dimensions.
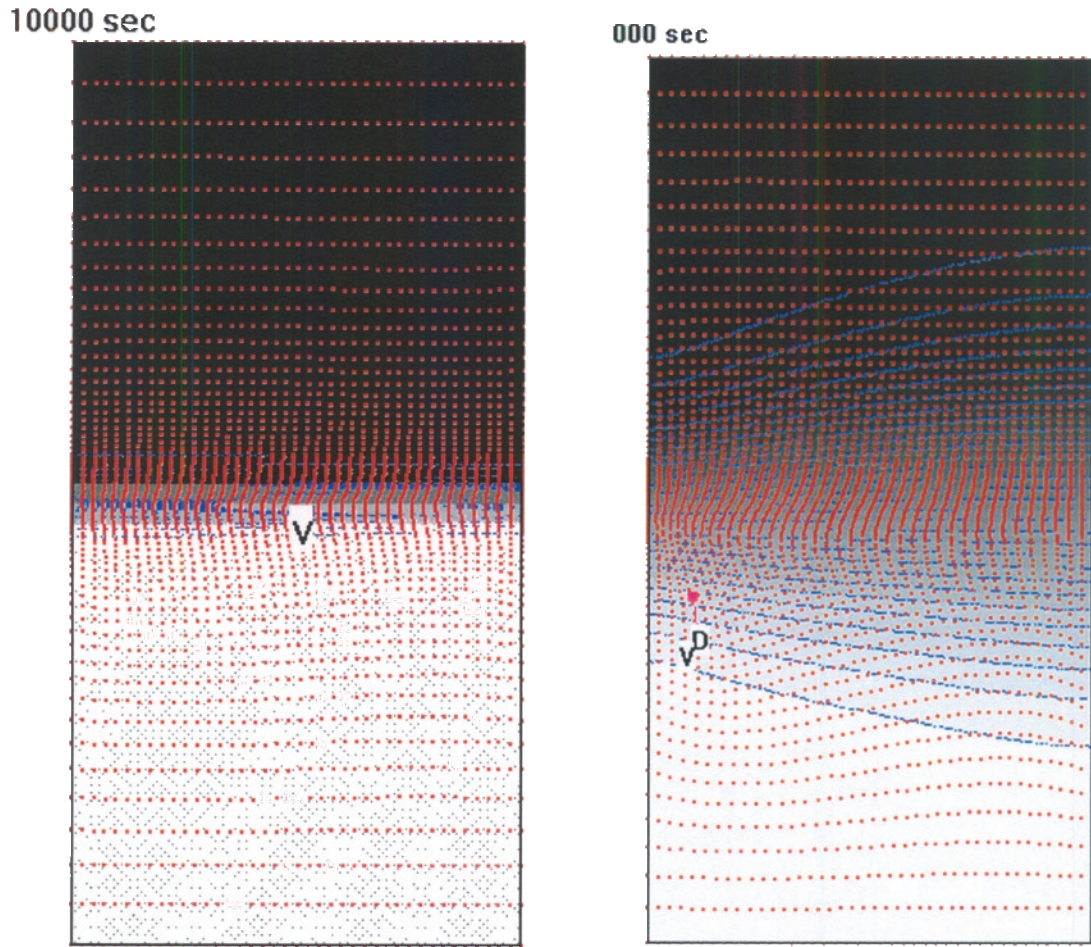
Figure 9. Left: The effect of a variation in k from 1.5×10^{-9} N to 1.7×10^{-9} N with with μ 0.002 Pa s increasing to 0.3 Pa s, after 10,000 s. Right: With k independent of T, k = 10^{-9} N but the diffusion coefficient increasing four times from right to left, after 1000 s.
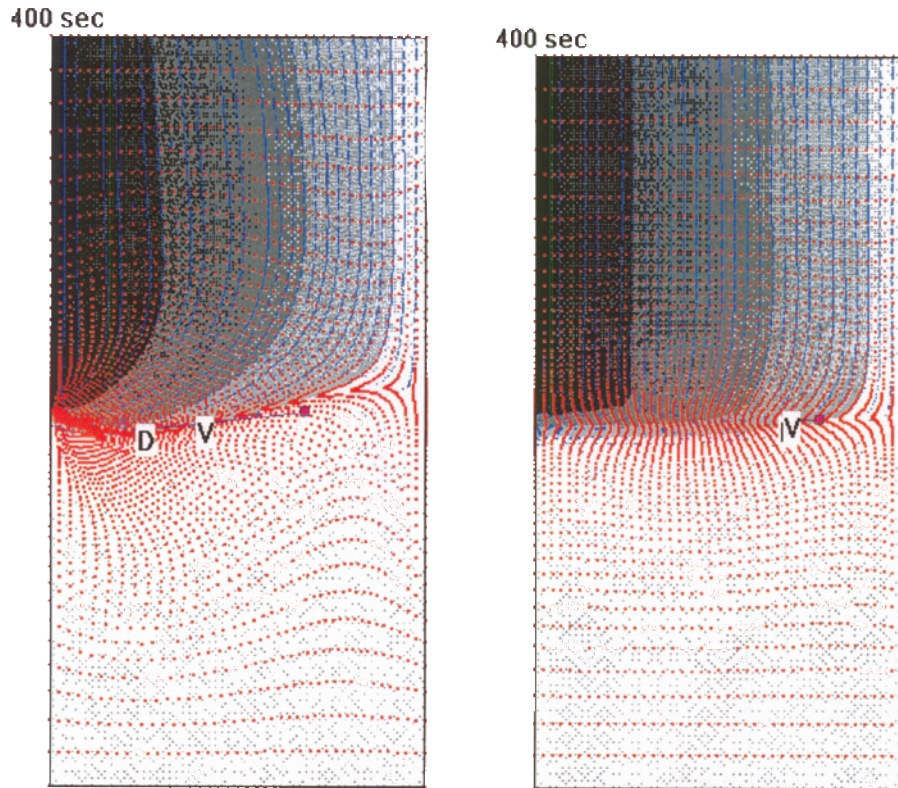
Figure 10. A gradient in polymer conversion along the transition zone with k = 10⁻⁸ N, T = 150 ˚C for full polymer conversion and T = 25 ˚C. Left: Diffusion coefficient is independent of T. Right: Diffusion coefficient increases with conversion.

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