Observation of a Reaction Front in the Bulk Catalytic Hydrogenation of a Polyolefin

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Background

We have previously reported the bulk hydrogenation of polymers.[1] Specifically, polybutadienes can be hydrogenated to good conversions under moderate conditions *in the absence of added solvent* by using molecular catalysts.[1] The most effective catalyst found for use in this bulk modification is the Crabtree catalyst,[2] $[Ir(COD)(py)(tcyp)]PF_6$ (COD = 1,5-cyclooctadiene, py = pyridine, tcyp = tricyclohexylphosphine).[3] While exploring the sensitivity of the hydrogen uptake rate to the physical form of the polymer, we observed an interesting phenomenon: When the polymer was fabricated as a full-density pellet, the hydrogenation produced a marked reaction front. The polymer was hydrogenated from the outside in. This paper presents our results on the behavior of the reaction front during hydrogenation and the nature of the interface produced in partially hydrogenated pellets.

Experimental Section

The commercial triblock copolymer polystyrene–polybutadiene–polystyrene (PS–PB–PS)[4] was provided by Shell Chemical Co. as Kraton D1102. The Crabtree catalyst was synthesized according to literature procedures.[2] The catalyst was dispersed in the polymer by vacuum evaporation of a solution of polymer and catalyst dissolved in dichloromethane. The resulting material was statically pressed at 80 °C in a mold treated with a commercial Freon-based mold release. The resulting pellets were roughly 2.5 cm in diameter and 2 mm thick.

Hydrogenations were performed directly on pellets placed in a commercial Parr minireactor, using documented safety procedures for working with high-pressure hydrogen. Pressures given are initial pressures. Osmium staining utilized vapor-phase osmium tetraoxide. Both hydrogen and osmium tetraoxide are hazardous materials. Anyone duplicating these experiments should be familiar with the associated hazards and should ensure needed precautions are met. NMR spectra and SEM micrographs were obtained on standard instrumentation. Measurements of inverse tensile compliance and reaction front position were performed on a custom instrument previously described by Gillen and co-workers.[5]

Results and Discussion

The material system studied consisted of the triblock copolymer containing 1% by weight Crabtree catalyst. Figure 1 shows the results of hydrogenation of a sample at 756 psig (sample B) and one at 40 psig (sample C) for 80 h each, as well as an unhydrogenated sample for comparison (sample A). Substantial differences between the center region and the outer regions of the cross-sectional view are visually apparent on both of the hydrogenated samples. The interface between the two regions appears sharp and has clearly moved to a greater depth on the sample hydrogenated at higher pressure.

When portions of the hydrogenated pellets were placed in $CHCl_3$, the inner region readily dissolved at room temperature, leaving an intact outer region. While PS–PB–PS dissolves in $CHCl_3$ at room temperature, its hydrogenation product, PS–H_2PB–PS, is resistant to dissolution because of the crystallinity of its midblock. This suggests that the observed interface in the partially hydrogenated pellets marks the position between fully hydrogenated and unhydrogenated regions of the sample. Solution NMR analysis of the room temperature extract from sample B indicated >97% unreacted PS–PB–PS with signals attributable to only trace $-CH_2-$. The intact outer regions dissolved upon heating to 60 °C. NMR analysis showed >95% PS–H_2PB–PS with a minor amount of unreacted double bonds. Further confirmation that the observed interface separated fully reacted and unreacted regions of the pellet was obtained by staining with osmium tetraoxide. The center (unhydrogenated) region stained preferentially. Again, a sharp demarcation between stained and unstained regions was observed.

Figure 2 shows a scanning electron micrograph of the interfacial region on pellet B. The elastomeric region on the left has contracted below the level of the semicrystalline material, presumably because of its different thermal expansion coefficient. The sharp nature of the interface is apparent. The results of measurement of the inverse tensile compliance[5] of the material moving in 100-μm steps along the cross-section of pellet B are plotted in Figure 3. An abrupt transition from stiff to compliant material was observed. It should be noted that the observation of a visual interface and its correlation with abrupt changes in the physical properties of the material do not necessarily require an equally abrupt transition in chemical composition. They are, however, strongly suggestive of such a transition.

The position of the interface changes with time at a given hydrogenation pressure. Data obtained by measurement of the depth of the interface versus hydrogenation time for pellet hydrogenation at 756 psig are presented in Figure 4. A clear $t^{1/2}$ dependence, where t is the reaction time, is observed. This coupled with the above observations indicates that the reaction rate is limited by the diffusion of hydrogen through the material to the reaction front. Once hydrogen diffuses to the boundary of fully hydrogenated polymer, it is rapidly consumed by reaction before it can further diffuse through unhydrogenated polymer.

This observation allows the diffusion process to be modeled as a one-dimensional, moving-boundary problem, in which the concentration of hydrogen at the pellet surface is equal to that in the surrounding gas phase and the concentration at the reaction front is zero. Solution of the diffusion equation for these conditions yields a prediction for the position of the interface, $X(t)$, of[6]

$$X(t) = \xi(2Dt)^{1/2}$$

where D is the hydrogen diffusivity and ξ is given by the transcendental equation

$$c_0 e^{-\xi^2/2} = (2\pi)^{1/2} b \xi \operatorname{erf}(\xi/2^{1/2})$$

Here c_0 denotes the concentration of hydrogen in the gas phase and b is the concentration of reactive double bonds. (In these experiments $b = 0.0133$ mol/cm^3.) The diffusivity in the hydrogenated polymer at 295 K can be calculated from the intercept of a log–log plot of the data (in conjunction with the known values of b and c_0[7]) and is found to be 1.77 (±0.25) × 10^{-7} cm^2/s. The error bar denotes our estimate for the 95% confidence limit and reflects the variation of the data about the least-squares line as well as the uncertainty in c_0.

Such heterogeneities in reactivity can be expected upon treatment of organic materials with reactive gases. For example, the oxidative degradation of organic cable materials has been shown to occur preferentially from the

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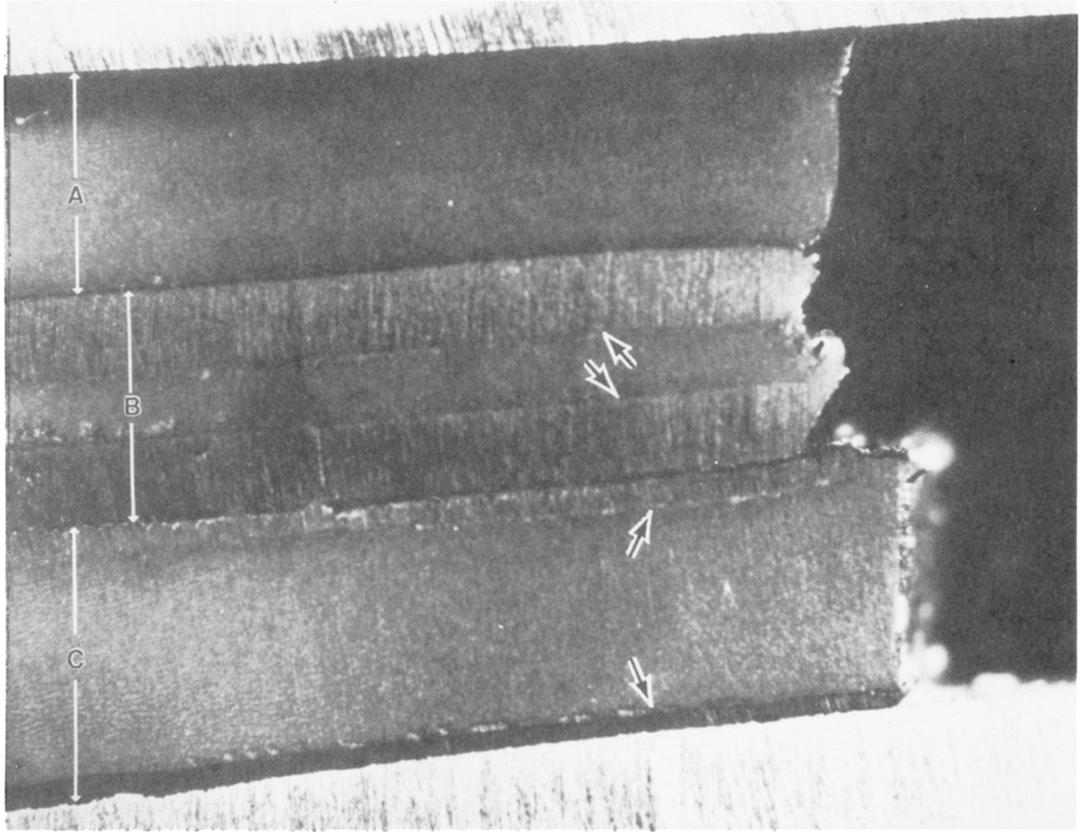

Figure 1. Photomicrograph of the polished cross-sections of three pellets of PS–PB–PS containing 1 wt % Crabtree catalyst: pellet A, unhydrogenated; pellet B, hydrogenated at 756 psig (initial pressure) for 80 h; pellet C, hydrogenated at 40 psig (initial pressure) for 80 h. Each pellet was originally 0.2 cm wide. Reaction front produced interfaces as indicated with arrows.

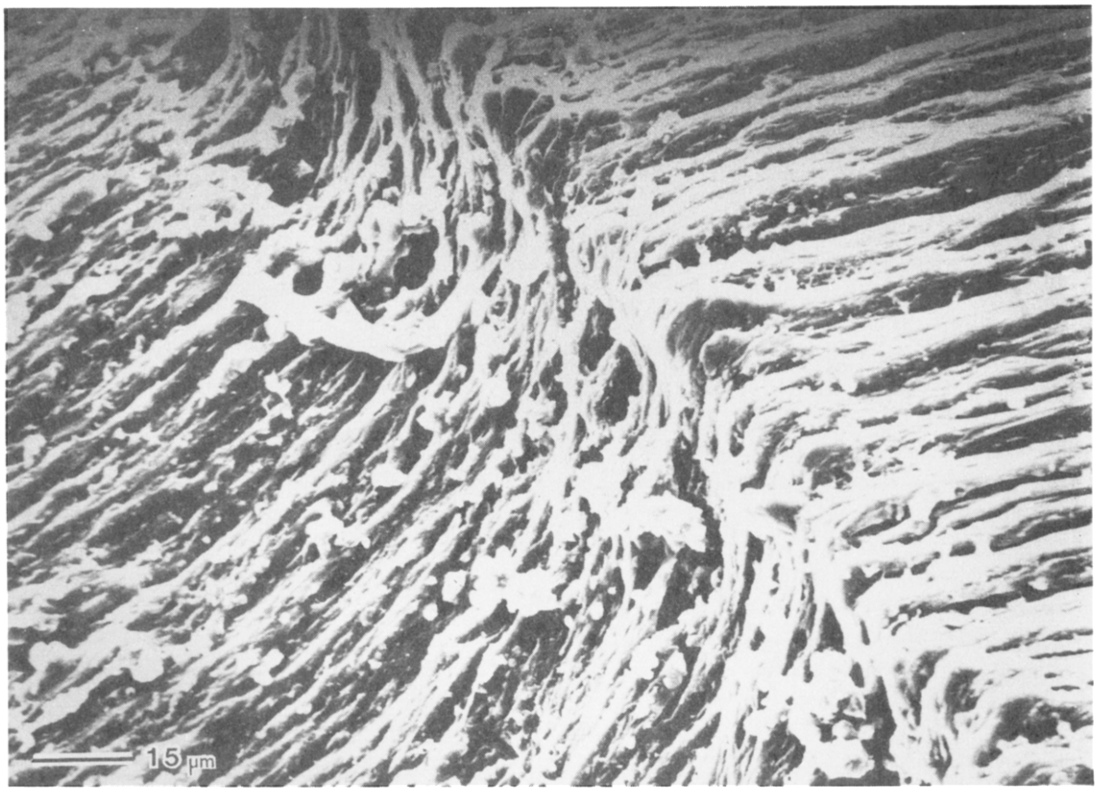

Figure 2. Scanning electron micrograph of the interface region between hydrogenated (right side) and unhydrogenated (left side) domains.

air–polymer surface.[8] In fact, the presence of a sharp reaction front has been described in the high-temperature fluorination of polyethylene[9] and in the gas-phase silylation of photoresists.[10] To the best of our knowledge, however, no previous report of catalytic reaction front chemistry such as that described above has been made.[11] Our efforts continue to further characterize the physical and chemical nature of the interface, to study other

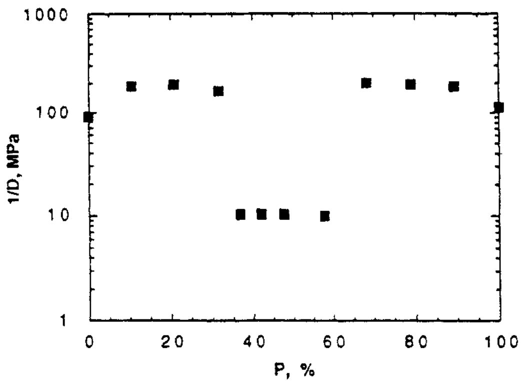

Figure 3. Modulus profile of the cross-section of pellet B. Data are plotted as the inverse tensile compliance of the material versus the probe position across the pellet's thickness direction.

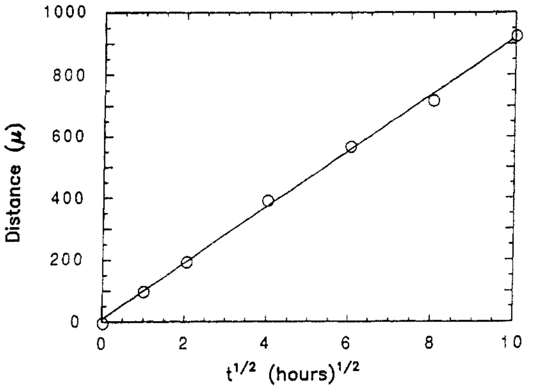

Figure 4. Position of the interface versus $t^{1/2}$, where t = hydrogenation time. The origin $d = 0$ is taken as the air–polymer boundary. The solid line represents the least-squares fit of the data.

catalytic chemistries involving gas diffusion through organic materials, and to explore the potential of catalyst infusion into preformed organic materials.

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