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A "Green" Technique for High Performance Elastomers

----Fundamental investigation for hydrogenation of nitrile butadiene rubber in supercritical carbon dioxide

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Summary: NBR hydrogenation, catalyzed by $OsHCl(CO)(O_2)(PCy_3)_2$ is investigated in supercritical carbon dioxide (SC-CO_2). The experiments were carried out in a volume-changeable SFT Phase Monitor with a view window. It was found that the catalyst could maintain steady activity in SC-CO_2 for a long time and no deactivation or decomposition of the catalyst was observed during the experimental operation periods. The reaction reached a conversion of 98% within 2.5 hours at 150°C. Increasing the temperature, specific area of NBR, CO_2 density and catalyst concentration favours higher hydrogenation degree, but the effect of hydrogen pressure is complicated and attention must be given to find the optimal hydrogen pressure. The results suggest that NBR hydrogenation could be possibly realized in SCFs in place of conventional organic solvents.

Introduction

The catalytic hydrogenation of acrylonitrile-butadiene rubber (NBR) is an important post-polymerization process resulting in a more stable and tougher derivative, hydrogenated NBR (HNBR), which is widely used in the automotive and oil drilling industry. Considerable effort and achievement have been made in developing homogeneous catalytic processes and technology for HNBR[1]. This has contributed to a successful industrial process for HNBR production. However, in the conventional operation, the procedures include the dissolving of the parent polymers in a large amount of organic solvent, reaction, and separation of the hydrogenated polymers and catalysts and recycling of the solvent. Due to the use of a large amount of organic solvent and expensive catalysts, complicated post-treatment and high production cost are inevitable. The complete removal of the organic solvent from polymers is not easy, which results in environmental concerns. Therefore, there has been a strong desire to develop a "green" hydrogenation process to upgrade the present technology. SCF technology is a hopeful way to realize this desire.

SCFs, especially SC-CO_2 (T_c=31.1°C, P_c=72.9atm), are receiving widespread attention because of their unique properties, such as tunable densities, viscosities, diffusivities, polarizability and dissolving power etc.[2] These unique properties have been exploited

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for tuning solubility, mass transfer, reaction rate and reaction selectivity in polymerization[3] separation/purification of polymers[4], micronization of polymers[5], ungluing, spray painting, foaming[6] of polymers, polymer modification[7], etc. The benefits of SCFs suggest that both increasing the solubility of H_2 and reducing the barrier of diffusivity will enhance the hydrogenation rate. The swelling capacity and the pressure-tuned properties of SC-CO_2 will facilitate the catalyst migration into the polymer phase and simplify the post-treatment. However, there appears to be no reported research involving the catalytic hydrogenation modification of polymers in SCFs, as yet.

The purpose of this paper is to investigate the possibility technically of NBR hydrogenation, catalyzed by $OsHCl(CO)(O_2)(PCy_3)_2$ in SC-CO_2.

Experimental apparatus and method

Apparatus The experiments were carried out in a volume-changeable SFT Phase Monitor with a view window supplied by Supercritical Fluid Technologies Inc. Fig. 1 shows a diagram of the SFT Phase Monitor reactor. The system consists of a 30mL capacity syringe pump, a high-pressure vessel with two quartz windows, a mixer, a light source, a video camera and a TV/VCR monitor. The pressure sensor is accurate to ±2psi with the operation range of 500-10,000psi. The accuracy of the temperature controller is ±0.5°C in an operation range up to 300°C. The color CCD camera is used to inspect the phase behaviour or reaction.

Material Ultra high purity hydrogen (oxygen free) and anaerobic CO_2 (Linde-Union Carbide) were used as received. The catalyst $OsHCl(CO)(O_2)(PCy_3)_2$ was prepared according to the literature method [8]. The NBR was provided by Bayer Inc. (Krynac 38.50) which contained 62 wt% butadiene (80% trans, 15% cis, and 5% vinyl C=C) with a Mn=70,000 and a polydispersity of 3.6.

Preparation of polymer samples Monochlorobenzene solution of NBR was cast on a piece of clean stainless steel mesh or plate. The supported polymer sample was dried at ambient temperature and pressure for 4 hours and then in a vacuum oven for 12 hours at room temperature to remove the solvent. The weight of the polymer was obtained by the weight difference between the supported sample and the support. The surface area of polymer film on the support was determined using a ruler (±1mm).

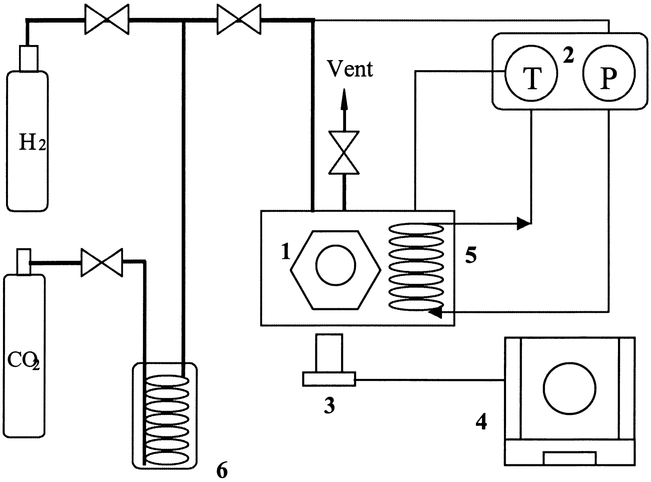

Figure 1. Schematic diagram of the SFT Phase Monitor Reactor.
1. Reactor, 2. Temperature controller and digital pressure indicator, 3. Color CCD camera, 4. Television monitor with VCR, 5. Heater mantle, 6. Cooler

Experimental procedures A certain amount of catalyst and a polymer sample were charged into the reactor. Then the system was sealed and degassed. The H_2 pressure was maintained at 2000 psi for 2 hours at ambient temperature. Then the system was depressurized to atmospheric pressure. Afterwards, a certain amount of liquid CO_2 was charged to the system. Then the system was charged with H_2 to the desired pressure. The magnetic stirrer was started and the polymer sample was soaked at low temperature for about 2 hours and then quickly heated to a desired reaction temperature. The reaction time is calculated from the point when the reaction temperature was reached. The hydrogenated polymer sample was analyzed by FTIR.

Experimental results and discussion

The reaction kinetic behaviour The apparent reaction behaviour in this system is affected by the hydrogen diffusion, catalyst diffusion and the intrinsic reaction kinetics. Figs. 2 and 3 show some reaction characteristics: 1) At these temperatures the conversions during the soaking period are almost negligible. 2) The conversion can reach 98% within 2.5 hours at 150°C. The apparent reaction rate increases with the temperature, and it has been found that no appreciable hydrogenation conversion occurred at temperatures below 100°C. 3) The reaction tends to be controlled by diffusion in the initial period of the reaction with higher thickness of the polymer film, and it tends to be dominated kinetically in the period of high conversion.

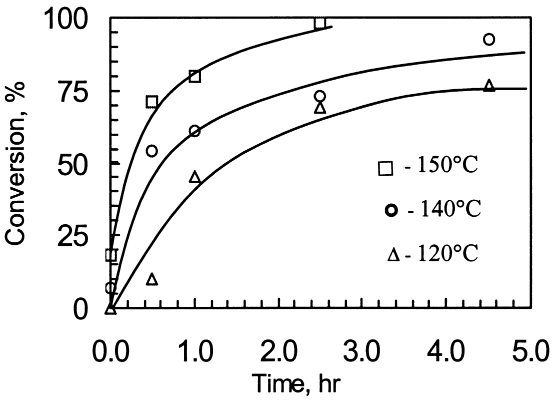

Figure 2. Effects of reaction time and temperature on NBR hydrogenation (total pressure: 6000psi; P_{H2}: 1150psig at 25°C; cat./NBR: 0.0769 wt/wt)

Effect of catalyst loading Experiments were carried out to determine the effect of catalyst loadings on the conversions. All reactions were conducted with the same reaction conditions (see Fig. 4). At lower catalyst loadings (less than 0.0769wt/wt), the conversion of NBR increases rapidly with the catalyst loading. However, the conversion shows little dependence on the catalyst loading as the ratio of the catalyst to NBR is higher than 0.0769 (wt/wt). This is possibly caused by reaching the saturation level of catalyst in SC-CO_2 or in the polymer. The upper limiting catalyst loading, beyond which no appreciable increase in conversion occurs, could be used as an estimation of a reasonable catalyst quantity for the hydrogenation, which in fact has been used in the rest of the experiments.

Effect of reaction pressure The influence of hydrogen partial pressures was investigated. All the experiments are carried out under a total pressure around 6000psig at 140°C. The results are shown in Fig. 5. The values of hydrogen partial pressures measured at 25°C are used in this figure. The conversions increase with the hydrogen pressures at lower hydrogen pressure. But the hydrogen pressure appears to have little influence on the conversion at higher pressures (>1150psig). A possible decrease in conversions was found with the further increase in the hydrogen pressures.

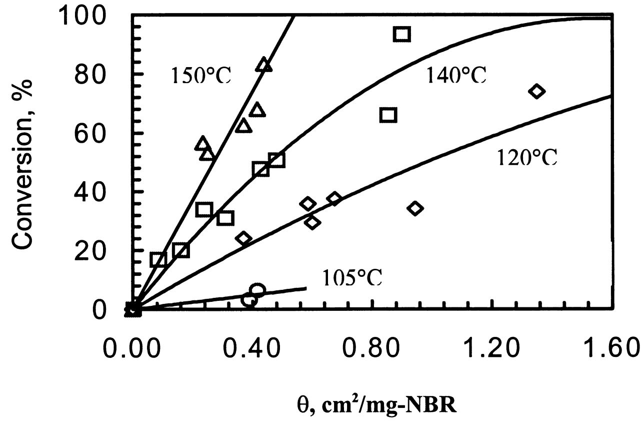

Figure 3. Effect of NBR film thickness on the hydrogenation. (reaction time: 2.5 hrs; total pressure: 6000psig; P_{H2}: 1150psig at 25°C; Cat./NBR=0.0769 (wt./wt.)

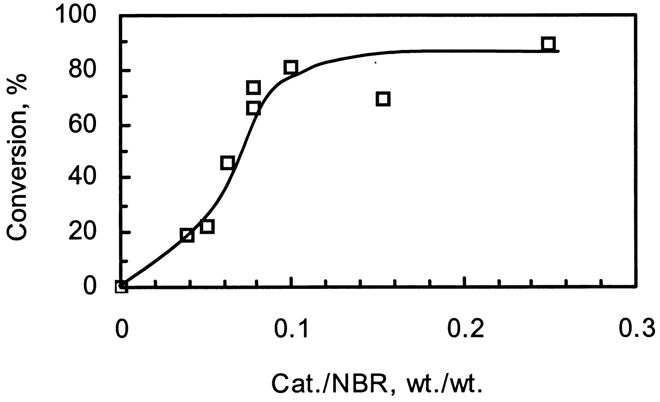

Figure 4. Effect of catalyst loadings on the NBR hydrogenation (140°C; total pressure: 6000psig, P_{H2}: 1150psig at 25°C; 2.5hrs)

The possible reasons for the hydrogen pressure effect could be due to several aspects. On the one hand, the increment of the hydrogen pressure will increase the hydrogen concentration which helps increase the hydrogenation rates. On the another hand, because of the fixed total pressures, higher hydrogen partial pressures mean lower CO_2 pressures, and consequently lower CO_2 density. The density of CO_2 is crucial for dissolving the catalyst and for swelling the polymer. The reaction may be slowed down quickly due to the decrease in CO_2 density. Over a range of low hydrogen pressures, the function of the hydrogen pressures overrides the effect of the $scCO_2$ density decrement. So the net result is that the conversion goes up with the increment of hydrogen pressures. When these two effects have similar influences on the reaction, the net results appear as if hydrogen pressures have little effect on the conversion. Another possible reason is when the supply of hydrogen is sufficient, hydrogen coordination to catalyst[9] is no more a significant factor. This was also found in homogeneous solution hydrogenation using the same catalyst[1], where the effect of hydrogen pressure was not significant when the pressure is higher than 62bar, close to the present result. With the further increase in hydrogen pressure and the decrease in CO_2 pressure, the migration of the catalyst from CO_2 phase into the polymer phase may be reduced significantly and result in the decrease in the apparent reaction rate and the conversion.

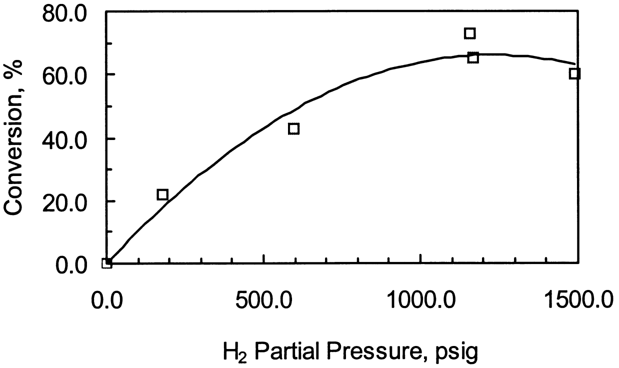

Figure 5. Effect of Hydrogen Partial Pressures on NBR Hydrogenation (2.5hrs; 140°C; total pressure: 6000psig; Cat./NBR=0.0769 (wt./wt.); hydrogen partial pressures was measured at 25°C)

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