

## Online monitoring of styrene butadiene copolymerization, including a final coupling reaction

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### Abstract

Automatic Continuous Online Monitoring of Polymerization reactions (ACOMP) was successfully used to continuously measure the anionic polymerization of styrene butadiene rubber (SBR) at the 20 L scale. The conversion was tracked, along with weight average molecular weight ( $M_w$ ), and low and high shear reduced viscosities (RV). The ACOMP data provided realtime reaction kinetics via conversion rates. After the initial reaction, the effects of the coupling agent were directly monitored by ACOMP. This showed a doubling in  $M_w$  over a short period of time and increases in RV commensurate with what one expects for random coils in a good solvent. The signatures of the various quantities versus time will be useful to establish the range of reaction trajectories that will produce a desired product. ACOMP can also monitor changes in these quantities as they occur, due to fluctuations in reaction conditions, such as pressure and temperature, addition of monomers, chain transfer agents, catalyst, crosslinking agents, etc. This leads to the potential for realtime reaction control which might include optimization of the endpoint of the first phase, triggering the coupling stage, and ending the coupling stage, among others. The ultimate goal of utilizing ACOMP data is to monitor and control polymer manufacturing at the industrial scale, leading to improved production efficiencies and minimum off-specification product. Additionally, ACOMP can be used for the discovery and scale up of new products as they are developed.

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The production of SBR via anionic polymerization is commonly used in production. This living type reaction leads to steady chain growth up to a desired molecular weight, at which point a coupling agent is added to link pairs of chains into single chains. The molecular weight of the product is a very important characteristic for determining its performance characteristics, because of its impact on processing and rheological properties.

ACOMP yields continuous data on these important characteristics of the reaction and resulting polymers. These polymer properties include conversion, molecular weight, reduced viscosity, and shear thinning viscosity. The principle of ACOMP uses a 'front end' to continuously and automatically withdraw a small stream from the reactor and dilute this to any desired degree with a chosen solvent or mix of solvents, while also performing such conditioning steps as phase inversion, filtration, removal of monomer, etc. The result is a continuous stream of dilute, analytical grade polymer solution, similar to what is produced offline in a quality control laboratory.

The 'detector end' of the ACOMP system continuously receives this diluted, conditioned sample stream and flows it through various desired detectors. In this application the ACOMP detectors that were used



included a multi-wavelength ultraviolet absorption spectrometer (UV), a five-angle static light scattering detector (LS), and low and high shear capillary viscometers. Other detectors are being researched for use in ACOMP, such as IR (infrared), refractometer, polarimeter (for chiral molecule detection), conductivity, dynamic light scattering, and Mie scattering.

It is important to note that *ACOMP is not a chromatographic method*, and it does not use chromatographic separation columns, such as in Gel Permeation Chromatography (GPC). Thus, it yields continuous average values, such as  $M_w$ , rather than the intermittent molecular weight distributions (MWD) provided by GPC. As a result, the polymer concentration levels of ACOMP are exactly the levels used in GPC; therefore, a complete GPC system can be attached to the output waste stream of ACOMP to obtain MWD and other separation information, in addition to the continuous ACOMP data.

This work outlines results obtained from the application of ACOMP to SBR reactions.

## Reaction information

The SBR reaction monitored was a conventional anionic polymerization of styrene (127.01 grams, 1215.3 mmol) and butadiene (508.02 grams, 9390 mmol) performed in hexanes at 14 wt% monomer using a catalyst of n-BuLi (4.4602 mmol) and ditetrahydrofurylpropane (2.933 mmol). After the polymerization was complete, to generate the base product, tin tetrachloride (1.100 mmol) was added to the reactor to couple the polymer chains.

## Results

Figure 1 shows raw detector signals (arbitrary units) for UV, SLS, and high and low shear viscometers, corresponding to the left-hand y-scale. The UV signal in Figure 1 does not return to its solvent value, due to scattering and absorption by the polymer that has formed. The true fractional conversion,  $f$ , is found by a procedure developed by Fluence Analytics, and the true conversion found by this procedure is shown on the right-hand y-axis. Figure 1 also shows the time when the reaction starts and when the coupling agent is added.

The signals in Figure 1 are all normalized to a scale of 1 and are interpreted as follows: The UV 265 nm signal decays monotonically, showing the conversion of the styrene into polymer. Due to formation of polymer after the reaction starts, the light scattering at 90° increases with respect to the increasing polymer mass, and it reaches a plateau during the first phase. Upon adding the coupling agent, the signal doubles rapidly. The low shear and high shear viscometers both follow the same trends as observed by the static light scattering detector. When the reaction begins, both viscosity signals increase until a plateau is reached. The addition of the coupling agent causes strong increases in both viscometers.



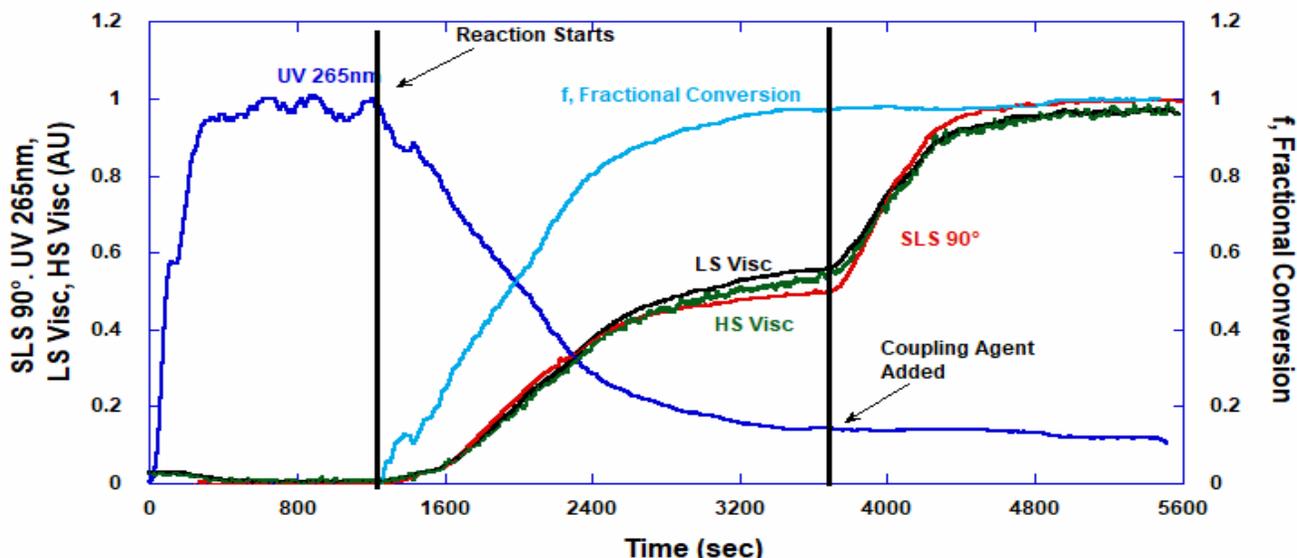


Figure 1: Raw ACOMP detector signals and corresponding fractional conversion

Figure 2 shows  $M_w$  and low and high shear RV as a function of time, including the coupling reaction.  $M_w$  was obtained from angular extrapolation (five angles; 45, 65, 90, 115, 135) to zero angle. It is noted that small corrections due to virial effects,  $A_2$ , may apply, as well as corrections for the use of  $dn/dc$ . Figure 2 reveals several features. First,  $M_w$  and both low and high shear RV increase monotonically in the first phase. This shows that the reaction is indeed of the 'living' type, where chains grow throughout the reaction. In contrast, in free radical reactions, chains are initiated, propagate, and terminate quickly, so that  $M_w$  decreases versus time. Examining the first and second plateau values gives  $M_{w,2}/M_{w,1} = 1.94 \pm 0.06$ . Similarly, high and low shear RV increase in the first phase, again exhibiting 'living' type behavior of the reaction and increase after coupling.

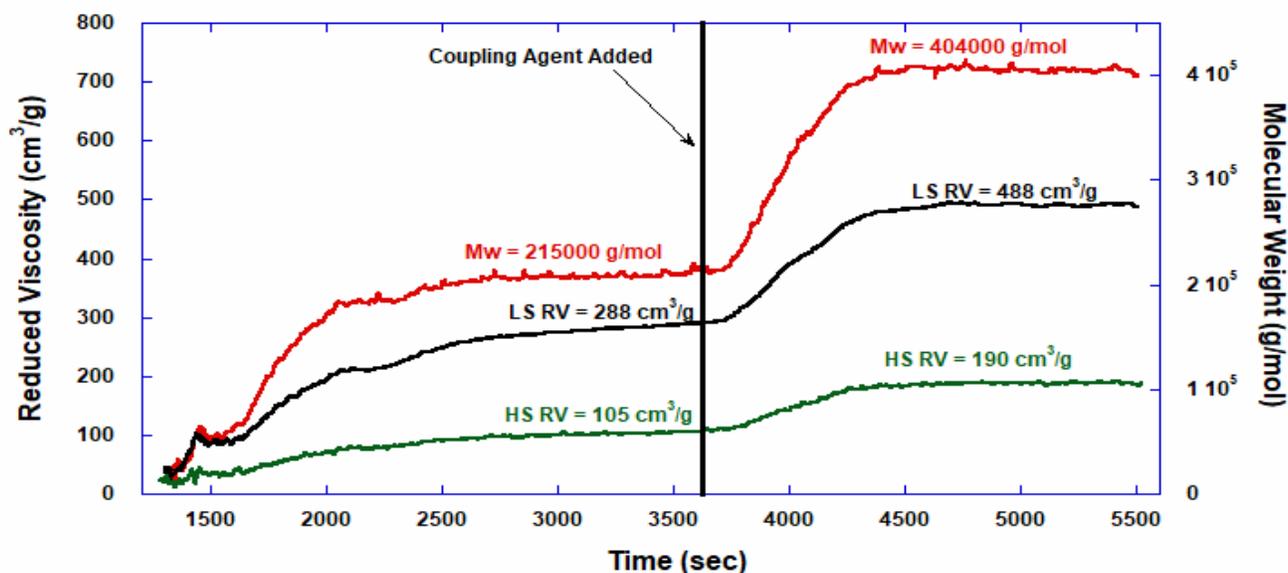


Figure 2: Mw and low and high shear RV from the data of Figure 1



Two sample aliquots were taken before and after the coupling agent was added to the reactor for characterization by conventional GPC standard calibration. The elugrams of each sample revealed two peaks of low and high molecular weight. The base product, shown in Figure 3, was determined to have a  $M_w$  of 132,000 g/mol for the low molecular weight peak and 300,000 g/mol for the high molecular weight peak. Since ACOMP is not a size exclusion method for characterization and analyzes the complete mixture of polymer for Weight Average Molecular Weight, the value is more heavily weighted to the higher  $M_w$  species, thus generating a value of 215,000 g/mol.

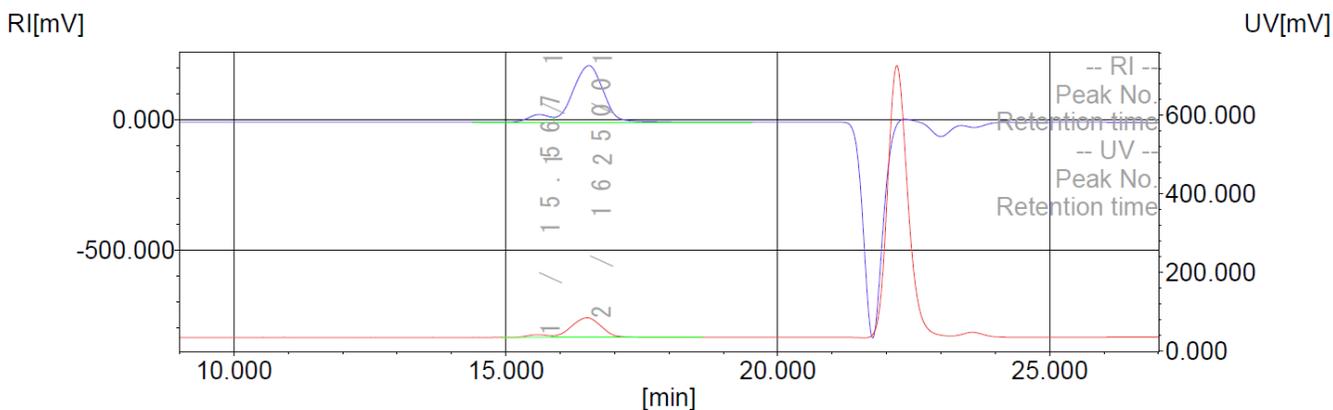


Figure 3: Elugram of Base product before coupling agent

The elugram of the post coupled product, shown in Figure 4, reveals that the low molecular weight species, with a  $M_w$  of 143,000 g/mol, has decreased as the population of polymer was coupled into the higher molecular weight species. The high molecular weight species reveals a  $M_w$  of 446,000 g/mol. Again, since ACOMP characterizes all polymers as a Weight Average  $M_w$ , the value is pulled down slightly due to the low molecular weight species to generate a value of 404,000 g/mol.

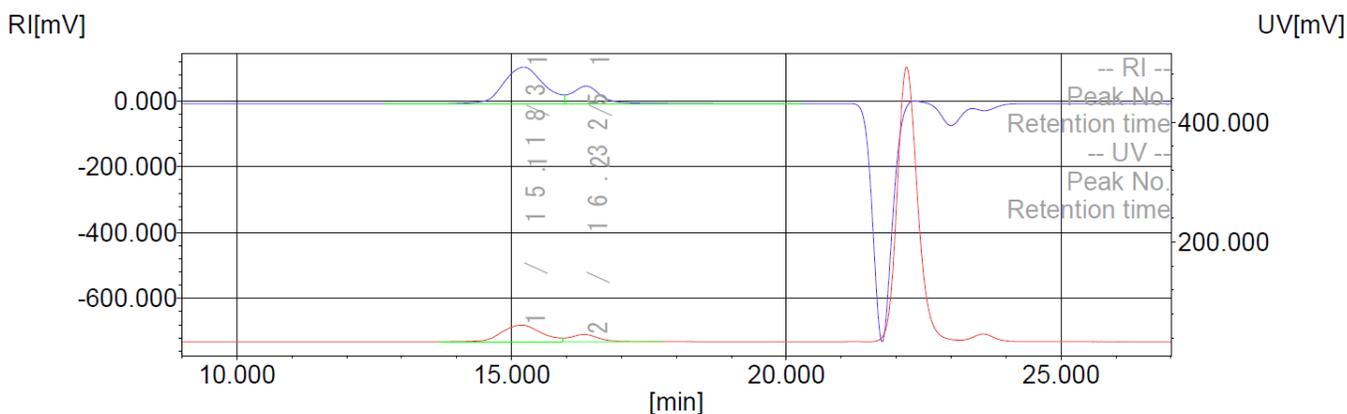


Figure 4: Elugram of product after coupling agent added

Interpreting the viscosity analysis in Figure 2 tells us that the plateau ratios are  $RV_{low,2}/RV_{low,1}=1.71 \pm 0.06$  and  $RV_{high,2}/RV_{high,1}=1.66 \pm 0.06$ . Using the Mark-Houwink equation (taking  $RV_{low} \sim IV$ , intrinsic



viscosity) yields an MH exponent of  $\alpha=0.73$ . This is in the range of expected values for random coils in good solvents.

$$IV = aM^\alpha$$

Plotting RV vs.  $M_w$  (Figure 5) shows that the MH exponent of  $\alpha=0.73$  is the same for both the first and second stage of molecular weight increase. There is a measurable shift in the molecular architecture observed between the two phases, whereby the pre-factor goes from  $a=0.0287$  in the first phase to  $a=0.0374$  in the second phase. With more data the change in the pre-factor 'a' may become a useful characterization of the coupling reaction.

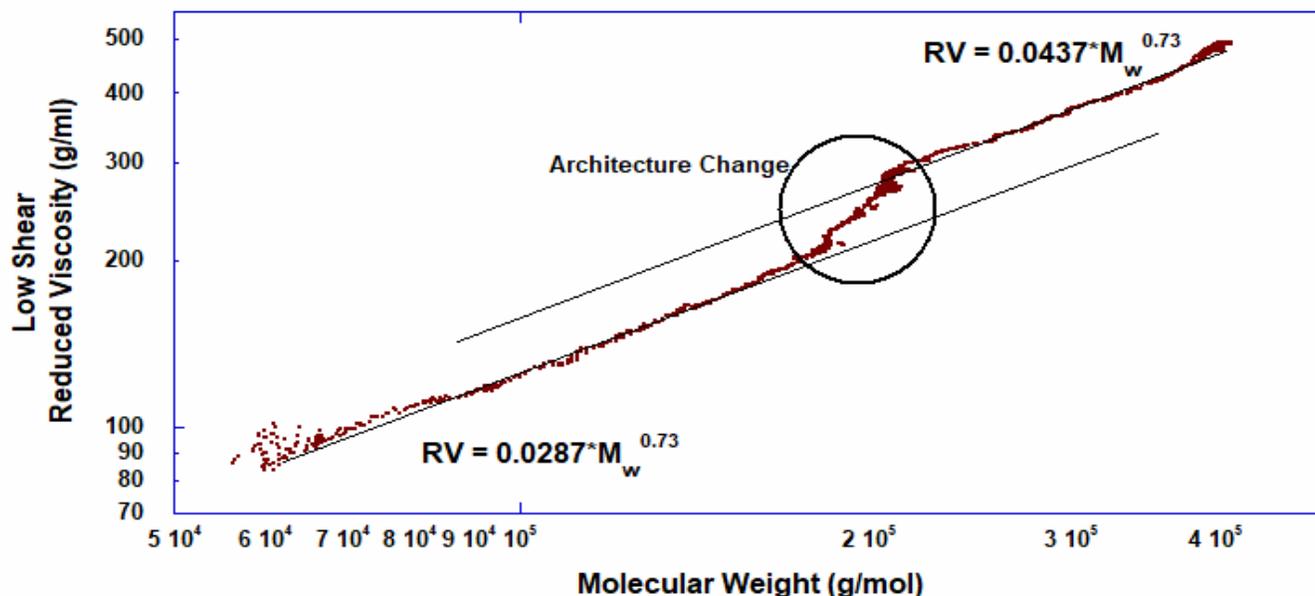


Figure 5: Low Shear Reduced Viscosity vs. Molecular Weight

Interestingly, there is a small but measurable drop in the percentage of shear thinning after the coupling agent is added, as displayed in Figure 6.

$$\% \text{ Shear Thinning} = 100 * \frac{LS RV - HS RV}{LS RV}$$

This suggests that the coupling reaction not only brings the benefits of higher  $M_w$  and intrinsic viscosity, but also measurably increases resistance to shear.



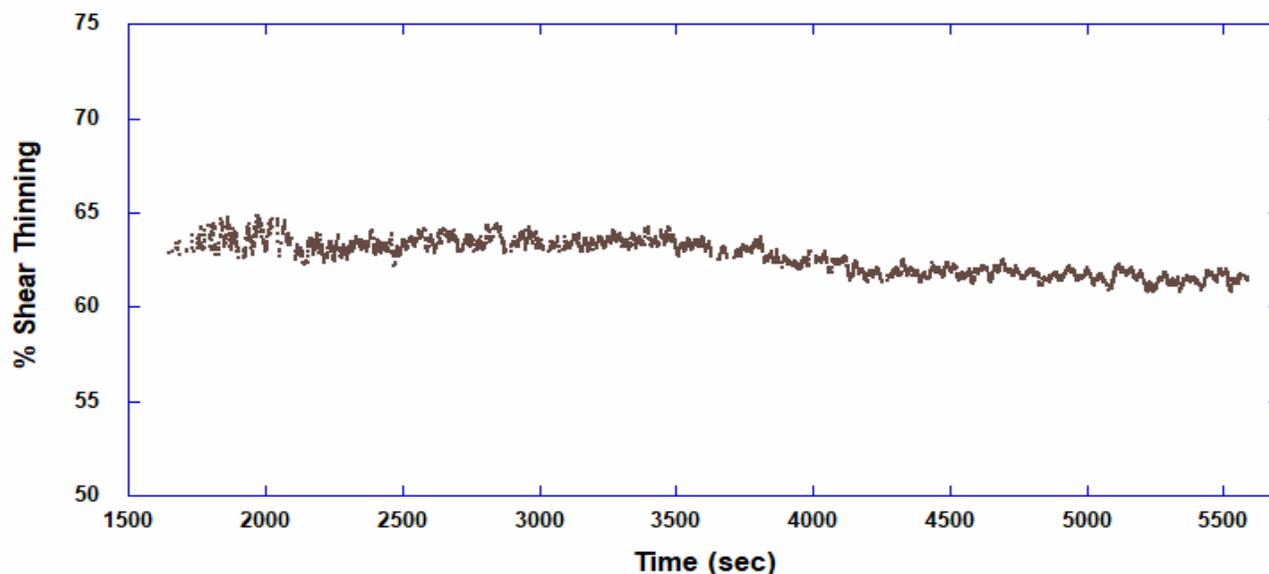


Figure 6: Percent Shear Thinning difference between High and Low Shear Reduced Viscosity

## Conclusion:

ACOMP has proven the capability of directly monitoring and characterizing polymer conversion,  $M_w$ , and RV of the polymers produced during a living, anionic solution based SBR polymerization process. This information is directly important with respect to characterizing the macromolecular polymer properties of  $M_w$  and RV, and it is also useful in providing insights into production rates and efficiencies, such as improving cycle time. This information also provides complementary information on the polymers produced which may lead to further correlations to important rheological properties of polymer end products such as Mooney and  $\tan\delta$ . The ultimate goal of utilizing ACOMP data is to monitor and control polymer manufacturing at the industrial scale, leading to improved production efficiencies and minimum off-specification product.

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