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INTRODUCTION

Diffusion effects are important in regular free radical polymerization systems. They lead to:

- A dramatic decrease in termination and propagation rates, and initiator efficiency
- Rapid increase in radical concentration and mixture viscosity
- Acceleration of polymerization
- Loss of temperature control

Questions:

- ▶ Do diffusional limitations also affect nitroxide-mediated radical polymerization (NMRP)?
- ▶ Are they as significant as in regular radical polymerization?

Answer:

The importance of diffusion-controlled (DC) effects in NMRP processes is rather controversial.

Several groups have assumed DC effects are significant and speculated that:

- The living character of the system is worsened (the linearity of average molecular weights versus conversion is lost and polydispersity increases)
- At mid-conversion levels, the system may exhibit regular radical polymerization features

Other groups considered these effects to be negligible due to lower molecular weight ranges typical of NMRP.

The issue needs to be clarified! How?

Literature Approach:

In most of the cases, researchers developed a mathematical model and included diffusional limitations mainly for termination (k_t) whenever there was some mismatch between experimental data and model predictions; usually an empirical equation indicating the dependence of k_t on conversion. **But was this mismatch really due to DC effects?**

Results inconclusive based on simulations (as most people rather "forced" models to agree with data due to higher number of available parameters).

Our Approach:

In order to clarify the above, we chose to look at a "worst case scenario" in order to "mimic" diffusional limitations.

"Worst Case Scenario":

- Create conditions where radicals are exposed to higher viscosities right from the outset. How?
 - ▶ **Add prepolymer at time zero.**

EXPERIMENTAL

Size exclusion chromatography (SEC) polystyrene standards or preformed nitroxyl-capped polystyrenes were added to a typical recipe for the bimolecular NMRP of styrene and the effects of their presence on polymerization rate and molecular weights were investigated.

The study was carried out at two concentrations of prepolymer (5%, 45%), different molecular weights (range from 5,000- 1,000,000) and two temperatures (120°C, 130°C).

TYPICAL RESULTS

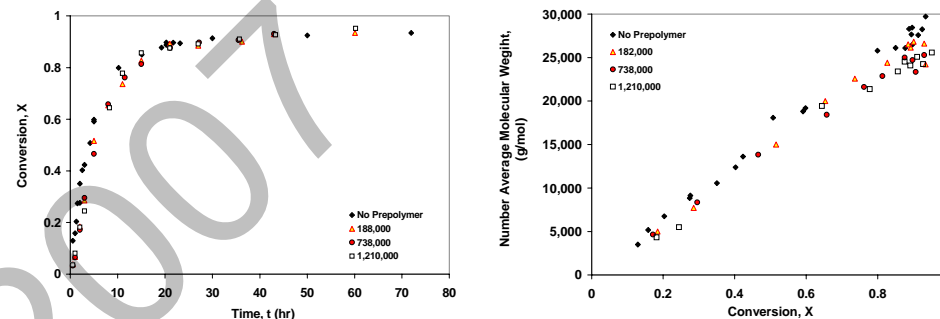


Figure 1. Effect of addition of prepolymer (5%) on rate and number average molecular weight. NMRP of styrene at 130°C, TEMPO/BPO=1.1 and $[BPO]_0 = 0.036$

MODELLING CORROBORATION

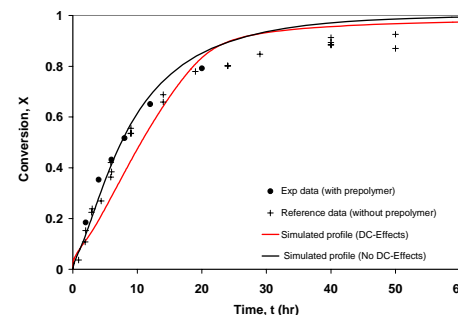


Figure 2. Comparison of experimental data and model predictions of conversion versus time for NMRP of styrene at 120°C, TEMPO/BPO=1.1 and $[BPO]_0 = 0.0192$; 45% prepolymer with $M_n = 17,400$

From all plots:

- Given the high concentration of prepolymer, it was expected that DC- effects would manifest clearly and early in the reaction profile but they didn't!
- Experimental data using prepolymer do not show much difference from the case without prepolymer (within experimental error)
- No significant improvement in the model by adding DC-effects

CONCLUDING REMARKS

- Overall, based on our investigations so far, DC effects seem to be insignificant.
- The low importance of DC effects in NMRP is related to the relatively short molecules (as compared to the chain lengths typical of regular radical polymerization), as well as to the typical operating temperatures being well above the T_g of resulting polymer.