SAND2019-10595C

Probing Heterogeneous Polymer Chain Dynamics Near the Glass Transition: A Solid State ^{1}H NMR Investigation

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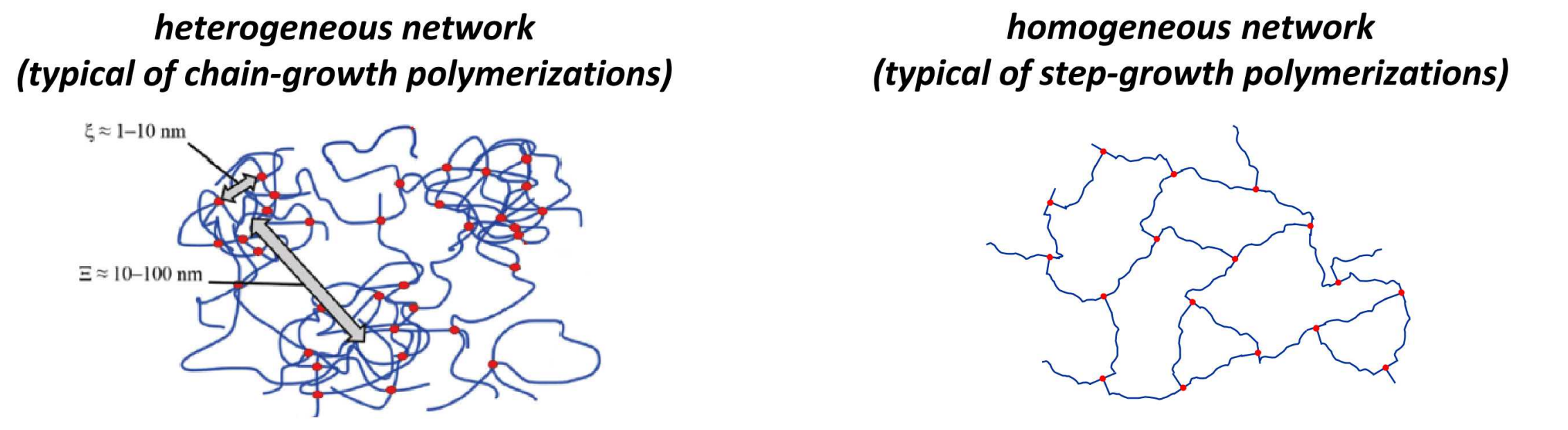
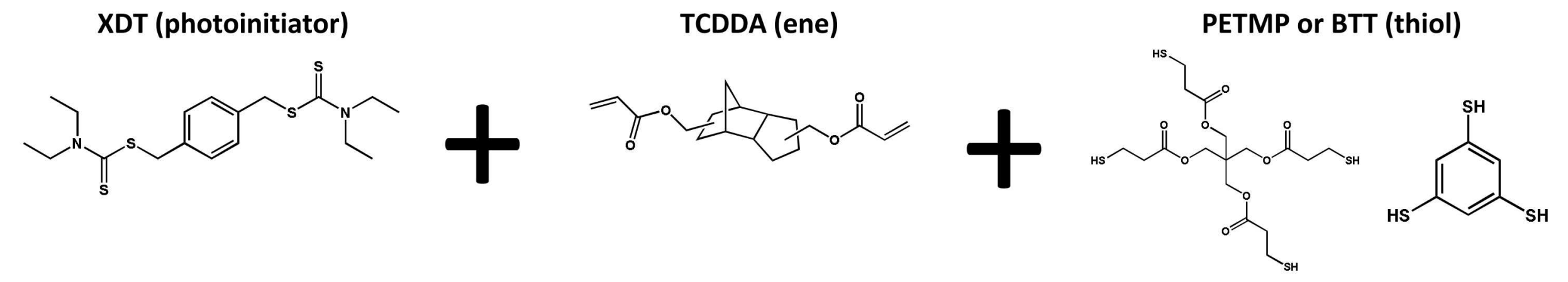
Introduction

Thermosetting polymers play an important role in adhesive, coating and composite applications. In such polymers, the introduction of permanent chemical crosslinks leads to the formation of stresses during curing. It has been proposed that polymer systems with large heterogeneities can be fully cured at temperatures well below the final glass transition temperature (T_g). The use of solid state ^{1}H nuclear magnetic resonance (NMR) spectroscopy can be used to directly probe the polymer chain dynamics near T_g. NMR then gives the polymer chain correlation times and activation energies (E_a) for the T_g process. Of specific interest is the impact dynamic heterogeneity has on the observed changes in the NMR line shape. By combining simulations and experiment, the line shapes were used to determine distributions in E_a for a series of thermosetting polymers with systematically varied heterogeneity.

Background and Theory





- Alkene (TCDDA) and photoinitiator (XDT) lead to chain-growth polymerization while thiol (BTT)-alkene chemistry leads to step-growth
- Ratio of alkene to thiol allows control over heterogeneity in the polymer ($r = [SH]_o/[C=C]_o$)

How do Dynamics Impact the ^{1}H NMR Spectra?

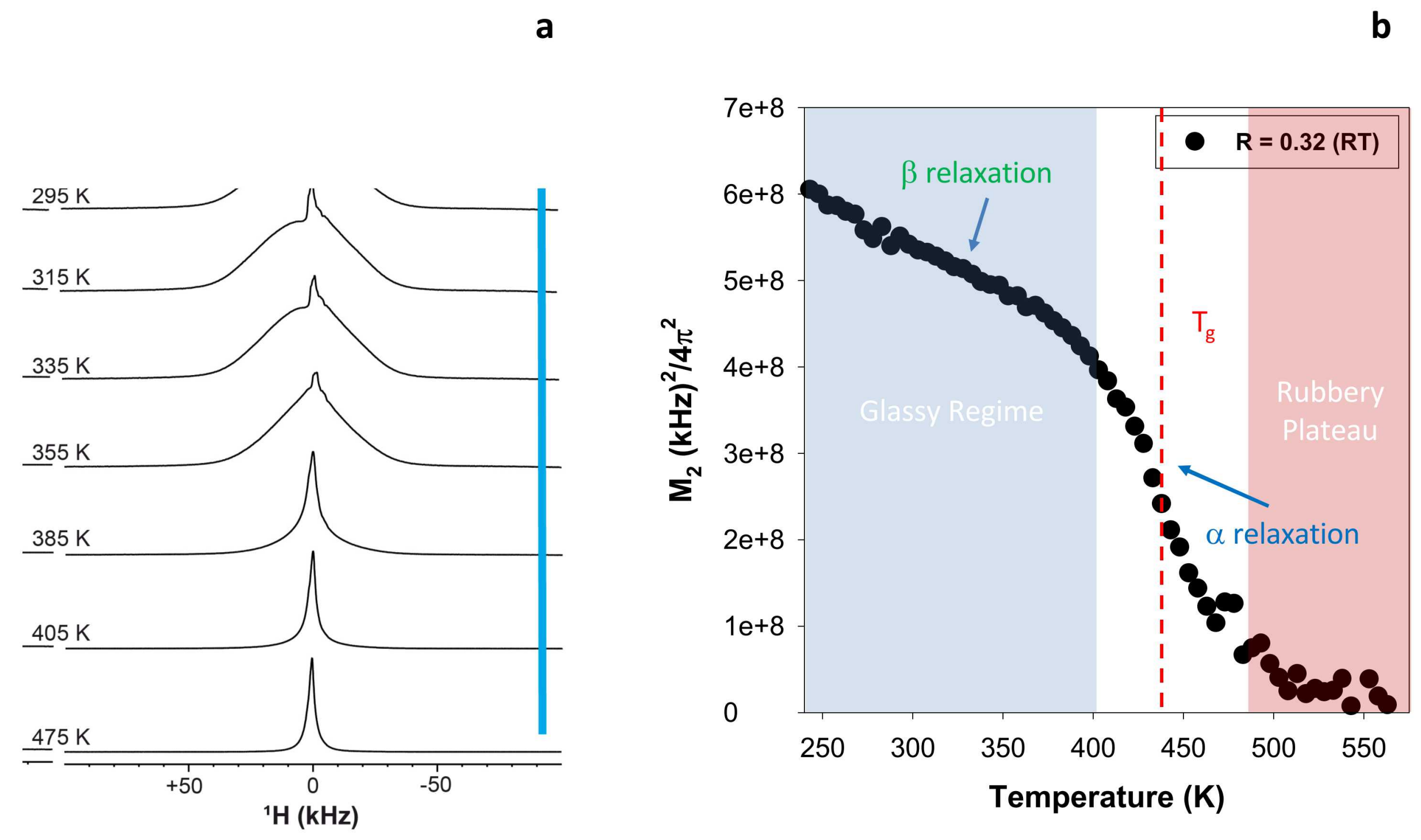
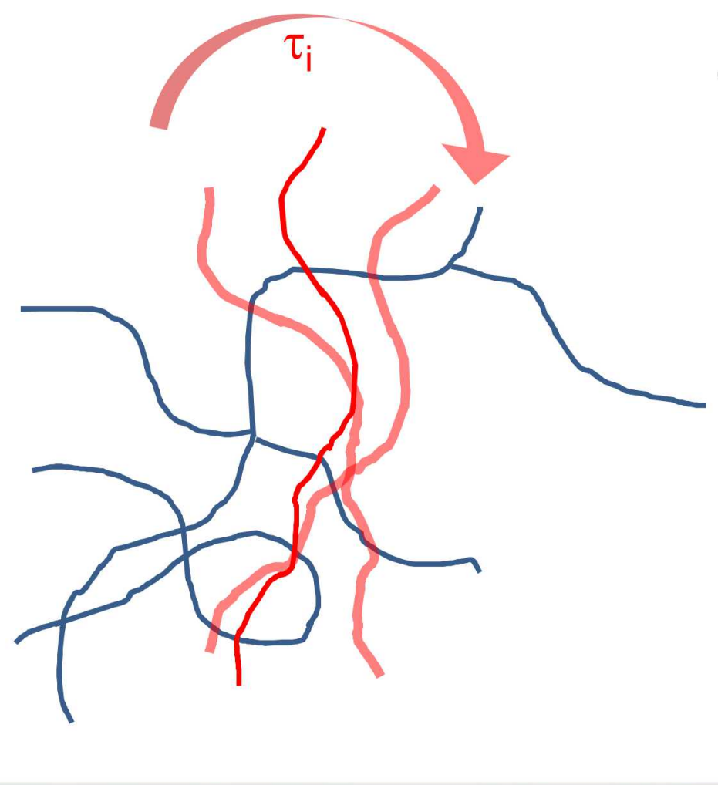


Figure 1. a) ^{1}H NMR spectra of thiol-ene system at different temperatures. b) Second moment of the NMR line as a function of temperature.

- Strong ^{1}H-^{1}H dipolar coupling leads to broader NMR lines
- Different dynamics lead to motional averaging of the dipolar coupling, represented by the second moment (M_2)

$$M_2 = \frac{3}{4}\gamma^2 h^2 I(I+1)\int_{-\delta v}^{+\delta v} J_0^{\ddot{v}}(v)\,dv$$



Single-Component Dynamics

$$\tau_c^i = \frac{1}{\sqrt{M_2}}\tan\left[\frac{\pi}{2}\frac{M_2^i - \langle M_2\rangle}{M_2^0 - \langle M_2\rangle}\right] \qquad \tau_i = \tau_0 e^{-E_a/RT}$$

Two-Component Dynamics

$$\begin{aligned} M_2 = \langle M_2\rangle &+ \left(\overline{\overline{M_2}} - \langle M_2\rangle\right)\frac{2}{\pi}\tan^{-1}\left(\sqrt{M_2}\tau_{c1}\right) \\ &+ \left(\overline{M_2} - \langle M_2\rangle\right)\frac{2}{\pi}\tan^{-1}\left(\sqrt{M_2}\tau_{c2}\right) \\ &+ \left(M_0 + \langle M_2\rangle - \overline{M_2} - \overline{\overline{M_2}}\right)\frac{2}{\pi}\tan^{-1}\left(\sqrt{M_2}\tau_{c3}\right) \end{aligned}$$

$$\tau_{c1} = \tau_0 e^{-E_a 1/RT}$$

$$\tau_{c2} = \tau_0 e^{-E_a 2/RT}$$

$$\frac{1}{\tau_{c3}} = \frac{1}{\tau_{c1}} + \frac{1}{\tau_{c2}}$$

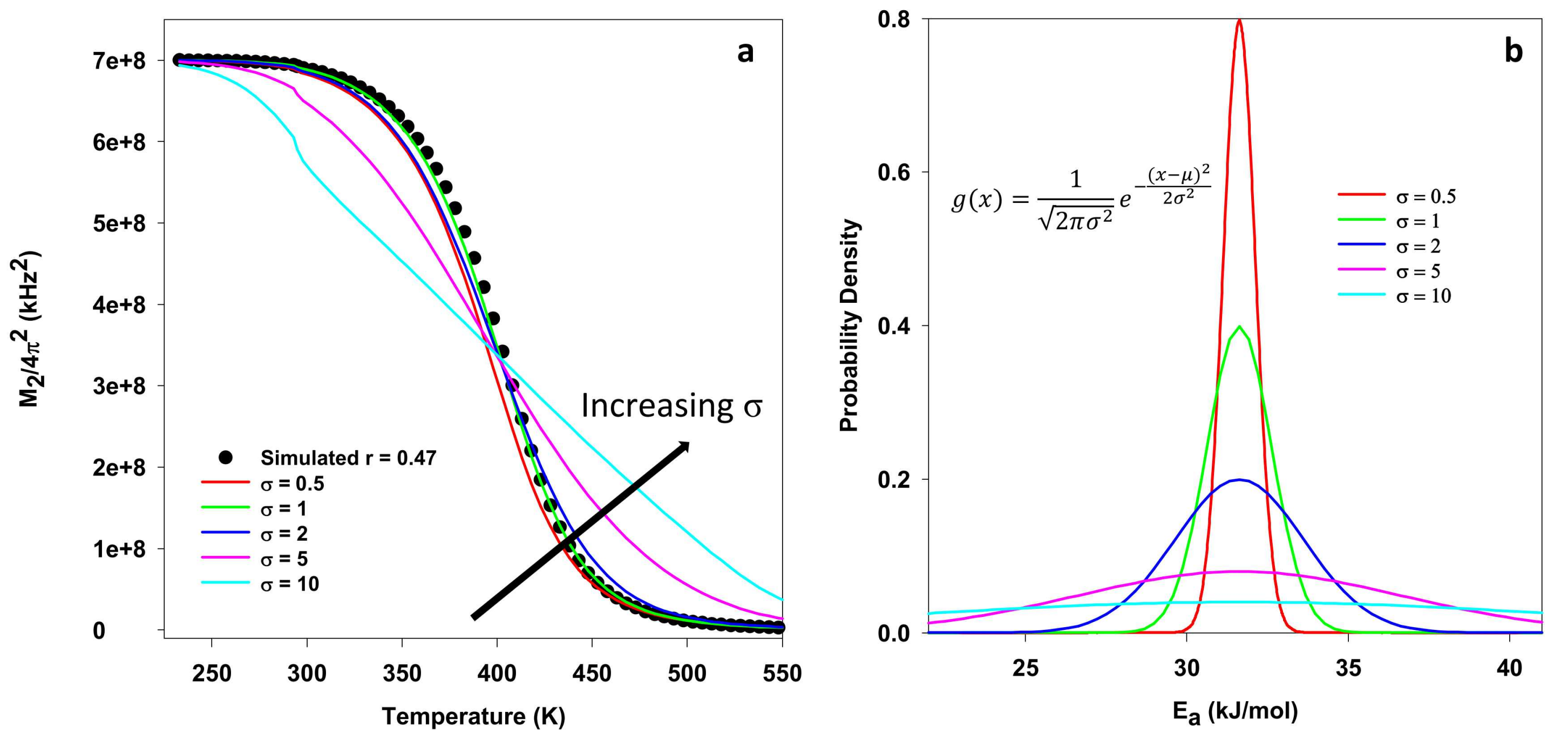
$\langle M_2\rangle = High\ Temperature\ Limit$

$M_0 = Low\ Temperature\ Limit$

$\bar{M}_2 = Lower\ Limit\ of\ 1st\ Transition$

$\bar{\bar{M}}_2 = Height\ of\ 1st\ Transition$

What is the Impact of Activation Energy Distributions?



$$g(x) = \frac{1}{\sqrt{2\pi\sigma^2}}e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

Figure 2. a) Simulated NMR second moments with increasing distributions in activation energy. Reference E_a and τ_o were taken as 31.6 kJ/mol and 5.9e-10 s respectively, calculated from experimental data at r = 0.47. Distributions in E_a were calculated by integrating over a probability density function and multiplying to the second moment. b) Probability density as a function of E_a with different sigma values. Sigma represents standard deviation.

- Distributions in E_a result in broader glass transitions, but the center point remains the same (Determined by E_a)

What is the Impact of Different Activation Energies?

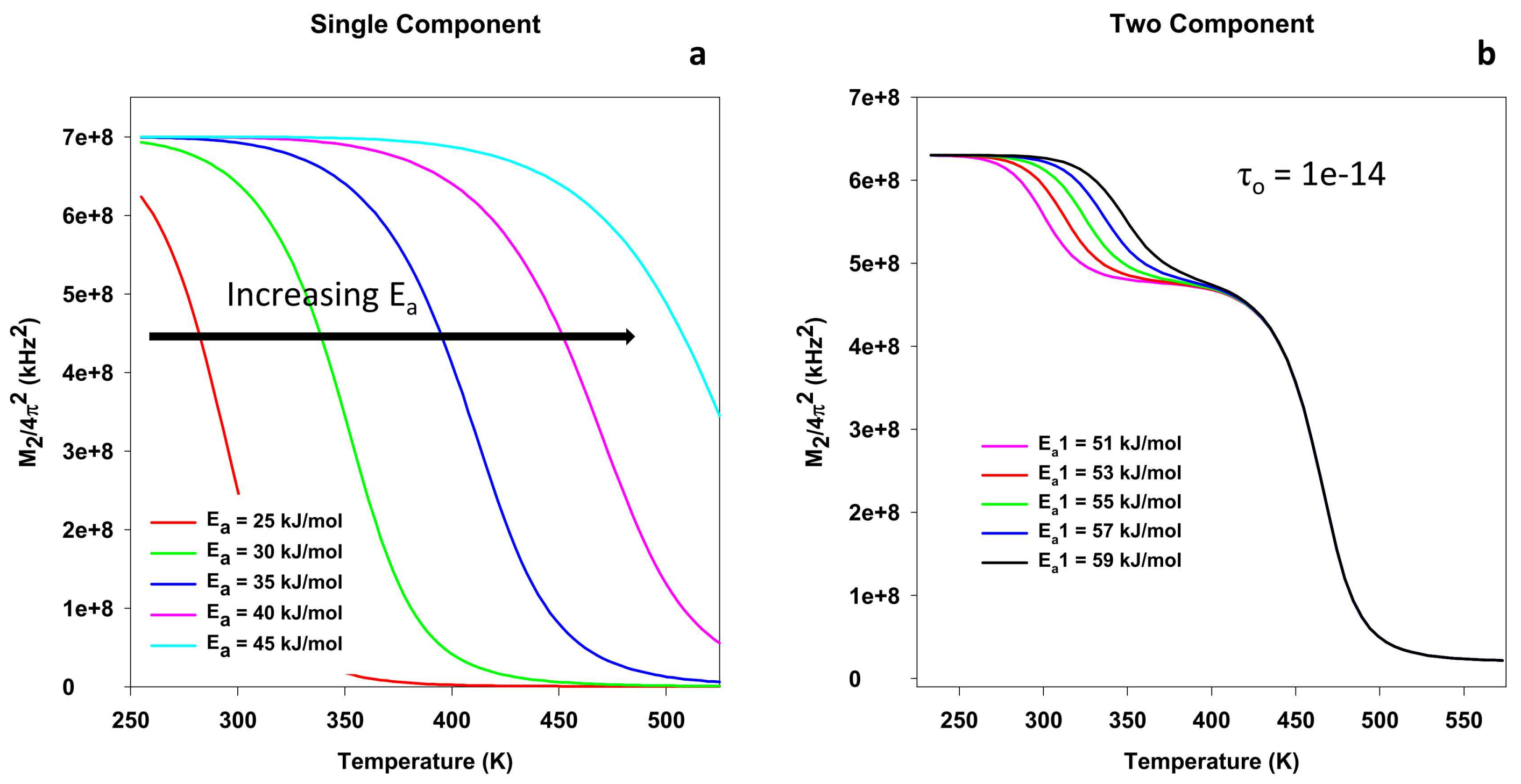


Figure 3. Simulated NMR second moments with different activation energies. a) Single-component model with τ_o taken to be 5.9e-10 s, calculated from experimental data at r = 0.47. b) Two-component model with τ_o taken to be 1e-14 s. Activation energy for the first transition, E_a1, is the varied parameter.

- Increasing E_a shifts the second moment plot, increasing the glass transition temperature

NMR Analysis of Thiol-ene Systems

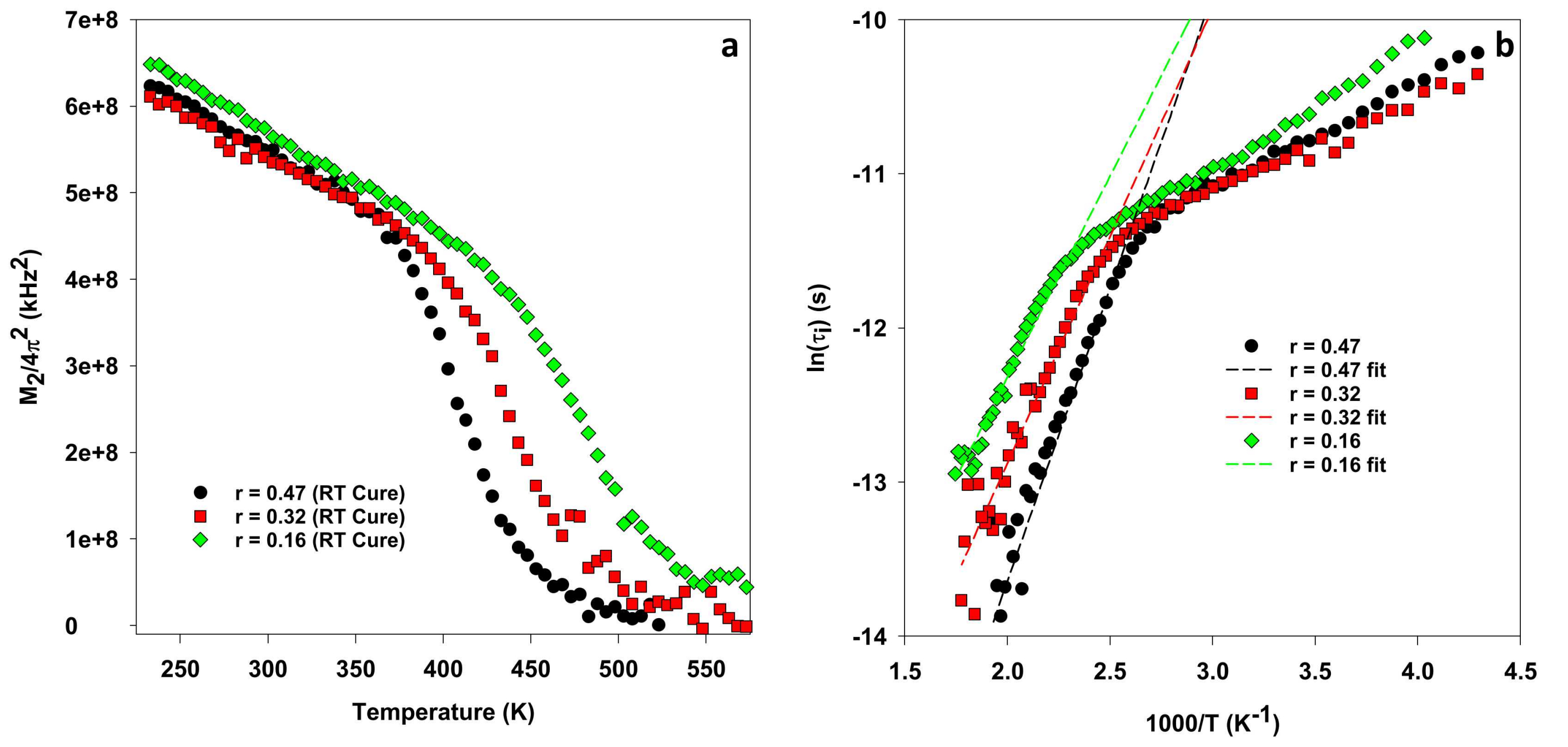


Figure 4. a) Experimental second moment data, calculated from NMR lines. Temperature is varied along the x-axis. b) Arrhenius behavior of thiol-ene systems. τ_i is calculated based on the single-component equation.

- Activation energy and correlation time can be extracted from experimental data using the arrhenius relationship

Simulation of Thiol-ene Systems

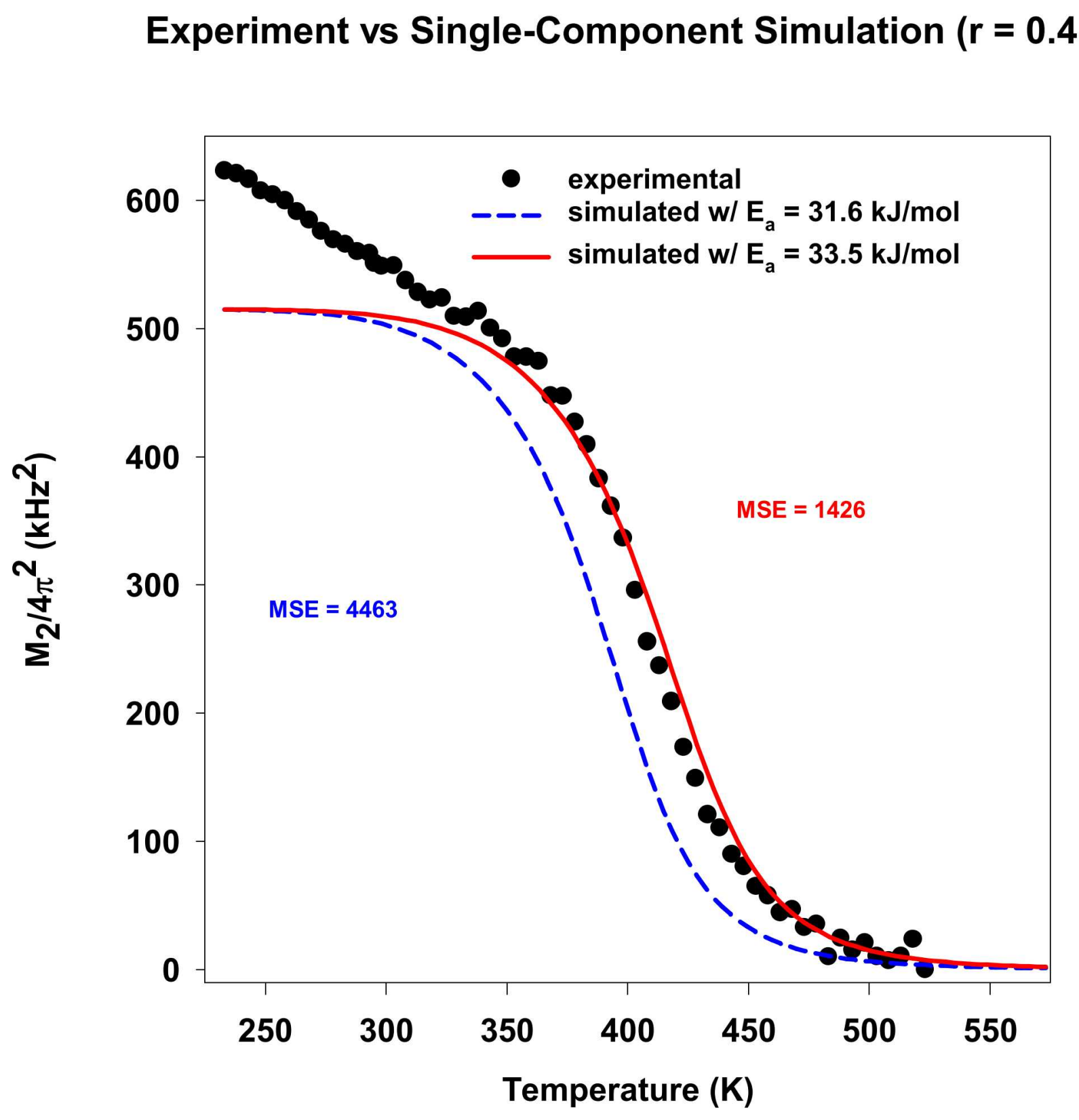


Figure 5. Simulated NMR second moments using the single-component model compared to experimental data.

- Initial simulation (dashed blue) was run using effective activation energy
- Best fit (red) required increasing activation energy and shifting the curve to the right

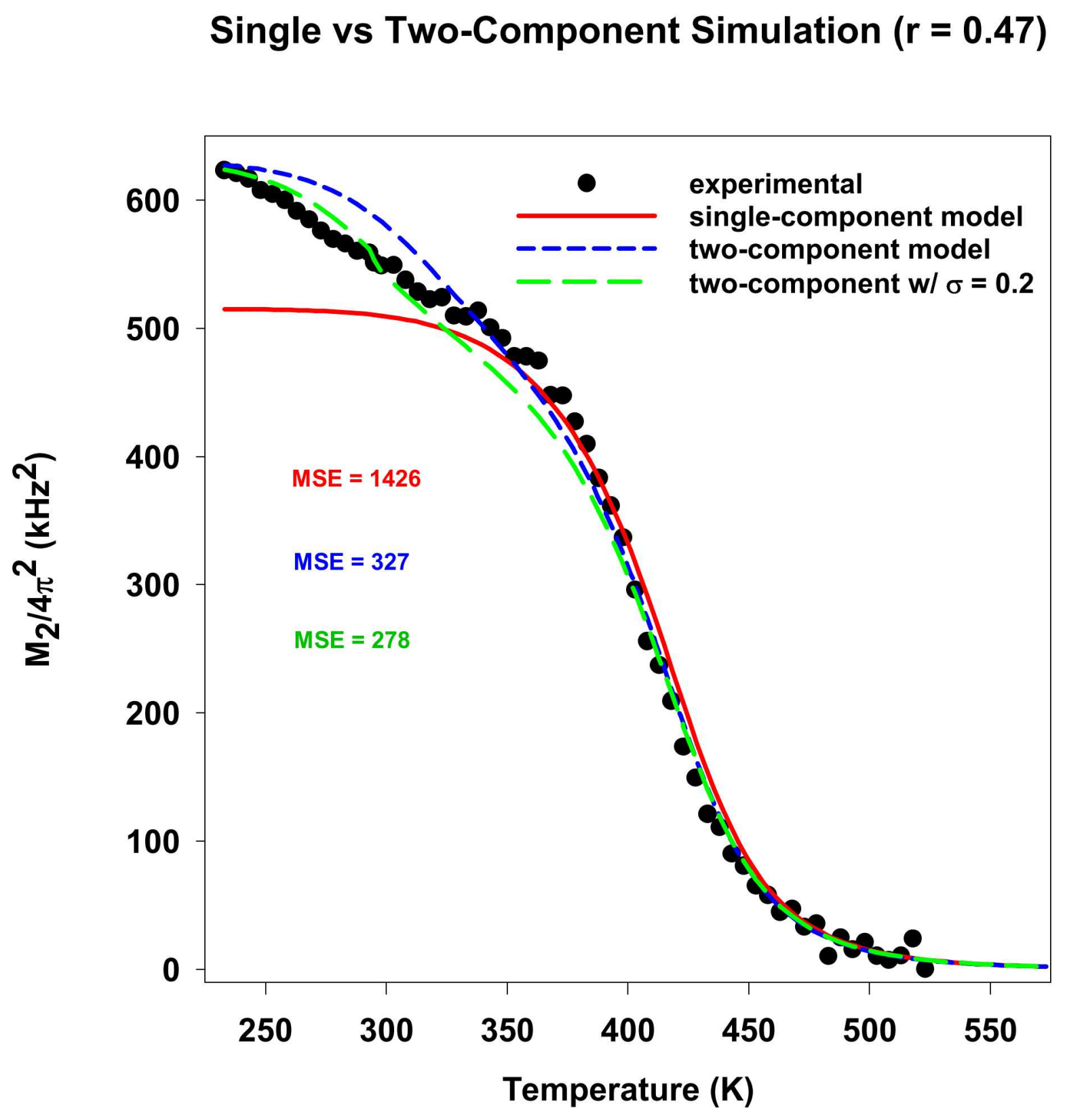


Figure 6. Simulations of NMR second moment using both single and two-component models.

- Two-component model better represents the β-relaxation region
- Best fit was created by introducing a distribution in the activation energy of the first transition (E_a1)

CONCLUSIONS

- **Increased dynamic heterogeneity leads to broad glass transition temperatures**
- **Dynamic heterogeneity introduces large distributions in E_a, which significantly change the NMR and second moment line shapes.**
- **Thiol-ene system is better represented by a two-component correlation function, due to the initial linear decay.**
- **Both models tend to under-predict the experimental data when using the effective activation energy and correlation time.**

Future Work

- **Complete NMR analysis of remaining samples (r = 0.08 and r = 0)**
- **Attempt to control heterogeneity in epoxy systems using the same methods**

References

[1] H.S. Gutowsky and G. E. Pake, "Structural Investigations by Means of Nuclear Magnetism. II. Hindered Rotation in Solids", J. Chem. Phys. 18, 162 (1950).

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Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywel
International, Inc., for the U.S. Department of Energy's National Nuclear Security Administratio
under contract DE-NA0003525. This work was funded through the Sandia LDRD program. Th
views expressed in the article do not necessarily represent the views of the U.S. Department o
Energy or the United States Government. SAND2019-3667C