MMa Bulk Polymerization and Its Influence on *In Situ* Resin Viscosity Comparing Several Chemorheological Models

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ABSTRACT: Earlier published rheological data of methyl methacrylate (MMA) heated and isothermally polymerized at temperatures between 50 and 80°C have been reanalyzed using three semiempirical models of viscosity advancement including a modified Boltzmann sigmoidal model, a microgel model for cure, and a first-order isothermal kinetic model. These alternative models possessed few fitting parameters and could be used without requiring more experiments to be run. For each dataset as a function of temperature, the analysis resolved time constants associated with both the induction time for polymerization and the rate of viscosity rise, which were inversely related to the polymerization temperature. We found the sigmoidal model the most robust to accommodate nonlinearities in viscosity advancement with radical polymerization of MMA. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1367–1371, 2011

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INTRODUCTION

Characterizing polymer advancement is industrially relevant, and the development of both mathematical and physical models to describe the physics of conversion, molecular weight changes, and heat transfer has been advanced. Recent reviews have treated dynamic conversion in bulk radical polymerization,[1–3] and specific models have been developed for polypropylene,[4] polyphenylene oxide,[5] polymethyl methacrylate (PMMA),[6–8] other acrylates,[9] polyamides,[10] epoxies,[11] norbornenes,[12,13] and low density polyethylene,[14,15] with the focus on plant efficiency and safety.[16,17] Similar rheological assessments during chemical reaction have also been performed with reactive extrusion.[16–18]

Simple phenomenological models have described these correlations, based on dynamic thermophysical property measurements. An excellent review article highlighted a range of different models of polymerization both in terms of viscosity advancement and thermodynamic heats of evolution.[19] Regimes of fluid viscosity have been linked to the physical structure of the monomer and the gel as conversion progresses, which has been characterized in recent efforts by Cioffi using mixtures of styrene and butyl methacrylate.[20] Much of the analysis is based on determining the Trommsdorff effect, the autocatalytic, polymerization-induced, conversion with intermediate stages defined primarily by diffusion and convection constraints.[3,20] The rate of change in viscosity at specific viscous ranges, and the induction times needed to trigger transitions from one zone to another are all measureable parameters and factors that can be included in the reaction engineering kinetics of polymerization.

Polymer sensitivity to the Trommsdorff effect has been sensed by differences in reactivity that are linked to dynamic viscosity changes. Determinations of dynamic viscosity parameters are achieved from fitting a power law model shown in eq. (1), where *b* is the power law exponent.[21]

At low values of *b*, there are no entanglements between polymerizing monomers; as *b* reaches intermediate ranges, polymerization is interpreted as constant with no diffusion limitations, and at high values of *b*, the Trommsdorff region is observed where rising viscosity blocks both heat transfer and mass transfer effectively.

$$\log \eta = \log a + b * \log t \qquad (1)$$

From an industrial processing perspective, the linkage between dynamic viscosity and material conveyance is a key for controlled polymerization.[20–22]

One reality with the power law model is that multiple regressions are required to characterize a single

dynamic viscosity curve, particularly if thermal runaway exists. As a result, interpretation is needed to resolve the individual stages of growth, and some resin mixtures clearly show a delineation in modes of behavior, whereas other filled resins with higher initial viscosity only show one slope in dynamic viscosity.[11] Formulation influences clearly affect reaction kinetics as well as how fast viscosity changes during conversion and can be resolved. Although the power law is simplest, the dynamic viscosity influences from a reaction exotherm or branching during conversion may have stronger influence on dynamic viscosity complicating its broader use. Alternative mathematical relationships to define dynamic viscosity might be also worth considering.

Halley and McKay[19] comprehensively summarized a large group of viscosity advancement models and provided links of what resins best fit these different empirical, semiempirical, and molecular conversion relationships. Alternative dynamic models include a first-order isothermal model [Eq. (2)] and the microgelation model [Eq. (3)],[23] which is obviously quite similar to the power law model. Both models also yield a time constant associated with conversion, and a second parameter tied to the initial viscosity.

$$\ln \eta = \ln A + t/\tau \qquad (2)$$

$$\log \eta = \log A' + b \log(1 + t) \qquad (3)$$

A third model we have deployed is a phenomenological sigmoidal model [Eq. (4)] that captures not only the nonlinear trend in polymerization but also can be adjusted using form fitting parameters to include an initial viscosity and an end-point asymptotic viscosity limit[24–26] as shown in Eq. (4).

$$\log \eta(t) = \log \eta_\infty + \frac{\log(\eta_0) - \log(\eta_\infty)}{(1 + \frac{e^{t-t_0}}{\Delta t})} \qquad (4)$$

The Boltzmann model has four fitting parameters, several with physical significance. η_0 is attributed to the initial viscosity of the resin. The terminal viscosity η_∞ is an upper bound in viscosity experimentally related to the torque limit of the viscometer. The induction time, t_0, corresponds to time required for viscosity to rise halfway between η_0 and η_∞ on a log scale. The other kinetic parameter, Δt, correlates to the inverse of the slope of the viscosity rise.[26] Increasing temperature results in a faster response in dynamic viscosity due to cure conversion and can be observed by the changes mostly in the time constants of the model. Theoretically, the sigmoidal model would predict an initial induction period of nearly constant viscosity followed by a transient period the slope of which is related to the reaction dynamics as advancement occurs. Both the induction period and the rate of slope rise in viscosity could be accommodated by adjusting the time constants. The model does not predict a viscosity reduction due to the initial cure exotherm but it successfully has tracked viscosity changes of several advancing resins including epoxies,[24,27] polyurethanes,[28] and acrylamides.[29]

We compared all of these other models re-evaluating prior published results from Sangwai et al.,[30] which could be extracted for reanalysis. The results follow.

EXPERIMENTAL

Previously published reaction conversion results for free radical bulk polymerization of methyl methacrylate (MMA) were identified using a near isothermal polymerization process and comparing the dynamic effect of conversion on viscosity and growing molecular weight were collected for reanalysis.[30,31] Briefly, those experiments determined conversion, $x_m(t)$, $M_w(t)$, and $\eta(t)$ for near-isothermal (NI) experiments using a Haake® viscometer (M5 osc, Haake® Mess-Technik GmbH, Germany) modified to function as a cup and bob reactor/viscometer. NI polymerization was one in which temperature is increased rapidly from a preheated condition of 43°C to a temperature ranging from 50–80°C and fixed thereafter. There is a short time excursion (probably less than 1 min) to reach this isothermal end-point temperature after which isothermal polymerization occurs.[30]

MMA was polymerized in the presence of 2,2′-azoisobutyronitrile (AIBN; SAS Chemicals, Mumbai, India) with initiator concentrations of 15.48 mol/m³ using an initial shear rate 10 s^{-1} and reduced to 0.01 s^{-1} with increasing conversion. The tabulated results of dynamic viscosity were exported into Origin 7.0 for reanalysis.

The datasets from the original manuscripts[30,31] were extracted for $\eta(t)$ and analyzed with the power law, first-order isothermal, microgel, and Boltzmann sigmoidal models described above for comparison and reported on in Table 1.

RESULTS AND DISCUSSION

Figure 1 includes the original measurements showing how $\eta(t)$ varies with polymerization temperature. At 50, 60, and 70°C, MMA exhibits some nonlinearity in semilog plots of $\eta(t)$, with the expected trend in reactivity. A direct comparison between the sigmoidal and the power law models for resin viscosity when polymerized at 70 and 80°C is shown in Figure 2. In simplifying the sigmoidal model, the initial viscosity (log η_0 (Pa s) = 0) and limiting

Near-isothermal 70°C					
Four-paramter Sigmoidal model with η_0 and η_∞ fixed		First-order isothermal model $\mathrm{Ln}\ \eta = \mathrm{Ln}\ A + t/\tau$		Microgelation model Log $\eta = \mathrm{Log}\ A' + b * \mathrm{Log}\ (1 + t)$	
R^2	0.993	–	0.96	–	0.968
log η_0 (Pa s)	0	A	0.0025 (Pa s)	A'	2.13E-13 (Pa s)
Log η_∞ (Pa s)	7.3	τ	8.43 min	b	7.38
t_0	60.79 min	–	–	–	–
Δt	3.94 min	–	–	–	–

viscosity of the crosslinked network, (log η_∞ (Pa s) = 7.3) were fixed. The limitation on log η ∞ (Pa s) = 7.3 is purely a torque constraint from the viscometer used and not a property of the polymer. Figure 3 compares all four different mathematical models for $\eta(t)$ described for the MMA dataset polymerized only at 70°C.

The comparison of the sigmoidal model using the datasets with the power law model led to some obvious differences. First, it was necessary to link several regimes of rheology with different power law exponents to force different zones of polymerization to mesh together on one dynamic viscosity curve as shown for resins polymerized at $T = 70$ and 80°C in Figure 2. The sigmoidal model more accurately describes a wider dynamic range of reaction-induced viscosity changes. Also, the determination of $\eta(t)$ at both the initial stages and at higher conversion was not captured. There are rheometer torque limitations in the high shear regime and at high conversion. More experiments at higher conversion are needed to validate the accuracy of each model. At the low end, η_0 for the simulated models

should more closely represent that of the monomer mixture before polymerization. Activation energies regulating monomer viscosity and reaction kinetics would suggest lower initial viscosity and higher reactivity with higher polymerization temperature.

Figure 2 clearly shows the trend of reactivity, but the low threshold of the measured viscosity range is much higher than the initial monomer viscosity estimated to be 0.6 cP (6 × 10^{-4} Pa s) at 20°C.[32] Huets et al. reported that initial methacrylate viscosity drops to 0.45 cP (4.5 × 10^{-4} Pa s) at 40°C[33] and as low as 0.33 cP (3.3 × 10^{-4} Pa s) at 70°C[33] with a reported activation energy of −9 kJ/mol.[34] Part of the discrepancy is the lag time needed to initiate each experiment. This problem is magnified at elevated temperature as the fixed time needed to place the monomer leads to less sampling with higher reaction rates. It is also reasoned that the parallel plate shear mode is less accurate. Better characterization of the initial viscosity could clearly yield a more accurate model overall.

The kinetic parameters Δt and t_o from the two-parameter sigmoidal models fixing η_0 and η_∞ (not
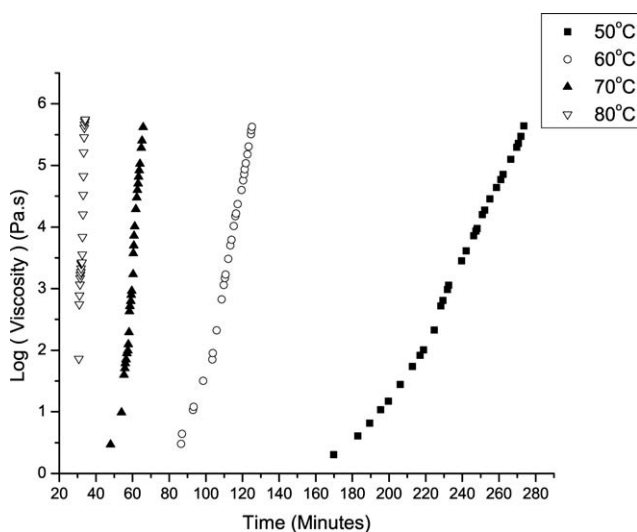

Figure 1 Data for the isothermal dynamic viscosity measurements with polymerization temperature (from Sangwai et al.[30,31]).
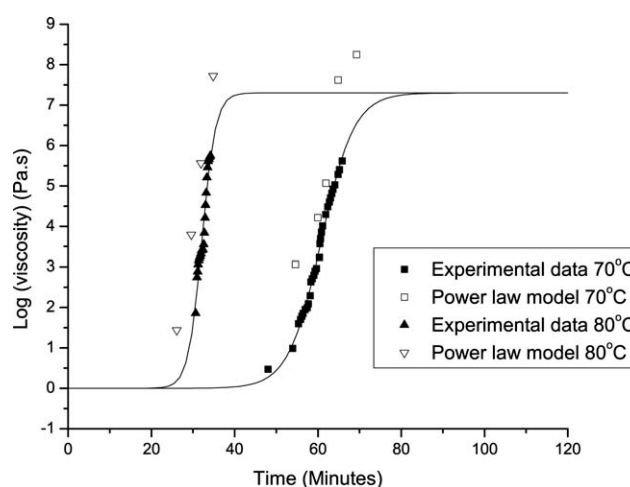

Figure 2 Power law model (open symbols) compared to the sigmoidal model fits (lines for polymerizing MMA combined with the raw data from Sangwai[30,31] (filled symbols).
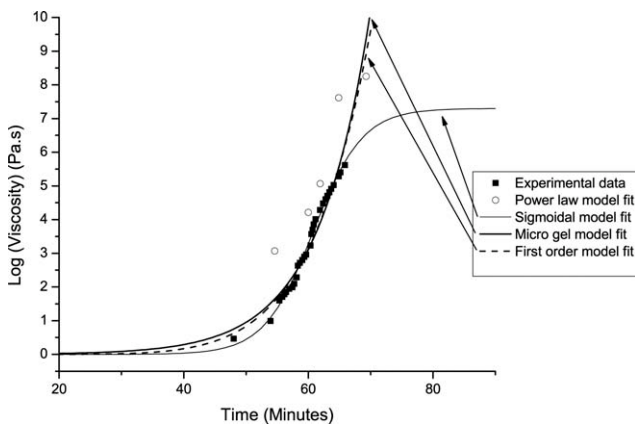
Figure 3 Four different mathematical models (first-order, microgelation, power law and sigmoidal) for isothermal polymerization data[30,31] at 70°C.

allowing them to be part of the variable fit) are correlated as a function of $1/T$ in Figures 4(a,b). Both parameters have a $1/T$ Arrhenius dependence sug-
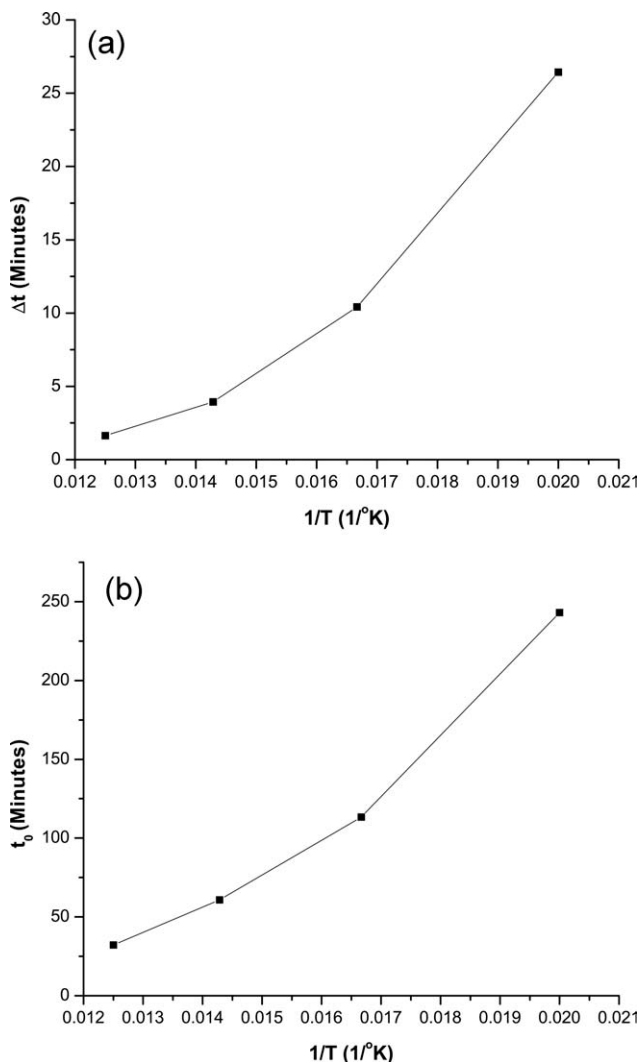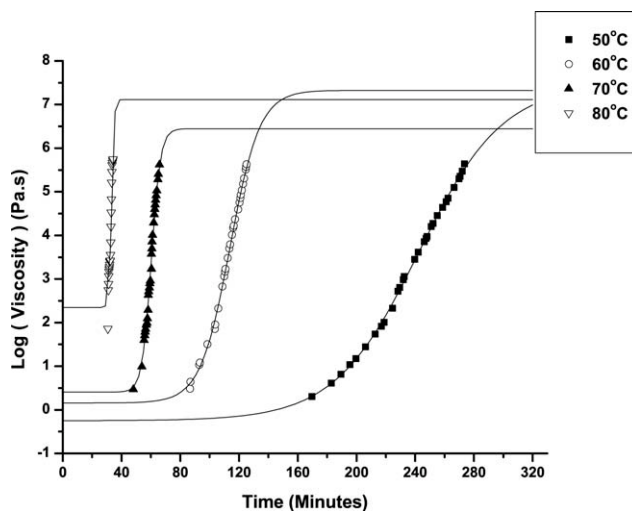

Figure 5 4 parameter sigmoidal model fit releasing the constraints that η_∞ and η_0 are fixed.

gesting an activation energy barrier exists to polymerize MMA. Neither parameter is linear over the 30°C differential in temperature in an Arrhenius analysis.

Removing the fixed constraints associated with η_0 (allowing it to vary as opposed to fixed parameter in the Sigmoidal Model) leads a counterintuitive temperature dependence on initial viscosity. Lower temperature cure corresponds to measurements of lower initial viscosity, which does not follow the Arrhenius trend noted by Huets at the monomer stage.[33,34] The increased reactivity at higher temperature coupled with the gap in viscosity measurements at earlier times in the cure profile may have led to early resin advancement and increased the uncertainty with resolving $\eta_0(T)$. If more data at the early stages of cure were available, that would help. Efforts to raise the accuracy of dynamic viscosity measurements offer the strongest chance to yield the most accurate picture of $\eta(t, T)$. Perhaps even more important is the need to link the new sigmoidal model to a reaction kinetics analysis model, so that $\eta(t)$ can be linked with regimes of polymerization. The rheometer seemed best suited for *in situ* tracking of instantaneous viscosity with conversion and might be less accurate at either end of the $\eta(t)$ spectrum. It is also appropriate to consider how the structure of the growing polymer affected its rheology, similar to work by Scorah et al. who varied initiator type and observed differences in the resulting branch structure.[35]

Figure 4 Variation of Δt (a) and t_o (b) with $1/T$.

CONCLUSIONS

Published data on MMA polymerization where $\eta(t)$ was measured *in situ* and previously analyzed using the power model were reanalyzed using three other

mathematical models. The Boltzmann sigmoidal analysis yielded three fits at each polymerization temperature, with 2, 3, and 4 fitting parameters. These were also compared with the microgel and the first-order isothermal models for polymerization. The sigmoidal analysis represented a wider range of dynamic viscosity. The other models represent a significant fraction of the dynamic viscosity during polymerization, but the nonlinearities are less fully captured. The future use of the sigmoidal model is tied to link the kinetic parameters to functional molecular models of resin advancement with more accurate viscosity measurements at all degrees of conversion. This alternative representation offers stronger hope that a more accurate model to describe thermal runaway during polymerization can be developed.

References

1. Oneil, G. A.; Torkelson, J. M. Trends Polym Sci 1997, 5, 349.
2. Cassagnau, P.; Bounor-Lagare, V.; Fernouillot, F. Int Polym Process 2007, 22, 218.
3. Odian, G. Principles of Polymerization; Wiley: New York, 2004.
4. Sarkar, P.; Gupta, S. K. Polymer 1992, 32, 2848.
5. Kuberkar, S. T.; Gupta, S. K. Polymer 1996, 37, 1243.
6. Achilias, D. S.; Kiparissides, C. Macromolecules 1992, 25, 3739.
7. Seth, V.; Gupta, S. K. J Poly Eng 1995, 15, 283.
8. Achilias, D. S. Macromol Theory Simul 2007, 16, 319.
9. Piguet-Ruinet, F.; Love, B. J. J Appl Polym Sci 2008, 107, 1523.
10. Wajge, R. M.; Rao, S. S.; Gupta, S. K. Polymer 1994, 35, 3722.
11. Love, B. J.; Piguet-Ruinet, F. J Appl Polym Sci 2007, 106, 3605.
12. Kessler, M. R.; Larin, G. E.; Bernklau, N. J Therm Anal Calorim 2006, 85, 7.
13. Larin, G. E.; Bernklau, N.; Kessler, M. R.; DiCesare, J. C. Polym Eng Sci 2006, 46, 1804.
14. Agarwal, N.; Rangaiah, G. P.; Ray, A. K.; Gupta, S. K. Ind Eng Chem Res 2006, 45, 3182.
15. Kiparissides, C. Chem Eng Sci 1996, 51, 1637.
16. Uhniat, M.; Zemlak, M.; John, J.; Szulc, R. Polimery 2003, 48, 709.
17. Kim, K. J.; Kim, B. K. J Appl Polym Sci 1993, 48, 981.
18. Jia, Y. X.; Zhang, G. F.; Wu, L. L.; Sun, S.; Zhao, G. Q.; An, L. J. Polym Eng Sci 2007, 47, 667.
19. Halley, P. J.; Mackay, M. E. Polym Eng Sci 1996, 36, 593.
20. Cioffi, M.; Hoffmann, A. C.; Janssen, L. Polym Eng Sci 2001, 41, 595.
21. Cioffi, M.; Ganzeveld, K. J.; Hoffmann, A. C.; Janssen, L. Polym Eng Sci 2002, 42, 2383.
22. Cioffi, M.; Ganzeveld, K. J.; Hoffmann, A. C.; Janssen, L. Polym Eng Sci 2004, 44, 179.
23. Malkin, A. Y.; Kulichikhin, S. G. Adv Polym Sci 1991, 101, 217.
24. Love, B. J.; Teyssandier, F.; Sun, Y. Y.; Wong, C. P. Macromol Mater Eng 2008, 293, 832.
25. Teyssandier, F.; Sun, Y. Y.; Wong, C. P.; Love, B. J. Macromol Mater Eng 2008, 293, 828.
26. Love, B. J.; Piguet-Ruinet, F.; Teyssandier, F. J Polym Sci B: Polym Phys 2008, 46, 2319.
27. Teyssandier, F.; Ivankovic, M.; Love, B. J. J Appl Polym Sci 2010, 115, 1671.
28. Teyssandier, F.; Love, B. J. Polym Eng Sci 2010, 40, 399.
29. Savart, T.; Dove, C.; Love, B. J. Macromol Mater Eng 2010, 295, 146.
30. Sangwai, J. S.; Saraf, D. N.; Gupta, S. K. Polymer 2006, 47, 3028.
31. Sangwai, J. S.; Saraf, D. N.; Gupta, S. K. Rheol Acta 2007, 46, 455.
32. Wikipedia. http://en.wikipedia.org/wiki/methyl_methacrylate. 2010.
33. Huets, J. P. A.; Roberts, G. E.; Biasutti, J. D. Aust J Chem 2002, 55, 381.
34. Huets, J. P. A.; Forster, D. J.; Davis, T. P. Macromolecules 1999, 32, 3907.
35. Scorah, M. J.; Tzoganakis, C.; Dhib, R.; Penlidis, A., Journal of Applied Polymer Science 103, 1340 2007.