Discussion of paper by L.-E. Chile, P. Mehrkhodavandi, and S. G. Hatzikiriakos, entitled 'Aromatic interactions in aryl-capped polylactides: A thermorheological investigation'

Citation: Journal of Rheology **61**, 1149 (2017);
View online: https://doi.org/10.1122/1.5008867
View Table of Contents: http://sor.scitation.org/toc/jor/61/6
Published by the The Society of Rheology

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(Received 10 October 2017; published 1 November 2017)

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Ralph Colby: In your Ref. 42, you apparently used UV-vis absorption spectroscopy to probe the extent and nature of the association of your aromatic ends groups. Do you think that studying UV-vis absorption spectra in the rheometer during shear or extension can tell us about how the flow may affect the aggregation state of these aromatic ends' groups as a function of shear or extension rate? Particularly for high molecular weight polymers, I wonder whether *in situ* UV-vis could explore the expectation that associations that break in flow may have difficulty finding another partner to reassociate with; can you comment on that?

Answer: A UV-Vis coupled rheometer would be very useful for determining the aggregation state of the aromatic end-groups. By looking for aggregation induced emission (AIE) we might be able to determine if the end-groups are simply pairing up or forming larger stacked aggregate structures under shearing conditions. It is expected that uncoupled chain ends in high molecular weight polymers would show a different absorption than those with coupled chain-ends, though the significance of this difference may depend on whether the chain-ends are forming pairs or clusters. Regardless, this would be a useful test to probe the ability of the chain-ends to reform their aggregates.

Evelyne van Ruymbeke: It is found that the horizontal shift factors used in order to build a mastercurve for the aryl-capped PLA show two different slopes, for the high and the low temperature data. This failure of time-temperature superposition principle, which takes place here at low frequency, has also been observed with other supramolecular polymers, in the frequency range where the stickers start to dissociate (i.e., the lifetime of the stickers = the inverse frequency of the oscillatory shear measurements), and has been attributed to the different T-dependence of the reptation process and of the dissociation mechanism.

Therefore, it would be interesting to compare the data presented for the system end-capped with the methanolpyrene [see Fig. 10(a)] to the data for the other systems. From the T-dependence of the shift factor, we could get more information about the stickers' influence and the activation energy of their association. Is this possible to see such a figure? Are the different slopes obtained in good agreement with the expected strength of the reversible bonds?

Answer: Horizontal shift factors for all aryl-capped PLAs show a similar two slope trend. As shown in Fig. 1, the differences in the slopes do indicate a difference in the activation of flow energies between the aryl-capped PLAs, the trends of which are parallel to that seen in the plot for the index of association (Fig. 12). Unfortunately, a literature search did not reveal useful data for us to compare the strength of these reversible bonds.

Dimitris Vlassopoulos: Based on the discussion in the paper, it becomes evident that the imperfect superposition of the linear viscoelastic moduli in Figs. 5 and 11 (which would be even more pronounced in a $\tan\delta$ or van Gurp–Palmen representation) may relate to aging effects. Still, it would help to know more about the shifting procedure used. In particular, was vertical shifting applied and if so what the relation to temperature dependence of the polymer density? This information would be useful for the reader.

Answer: Vertical shift factors were applied when creating master curves for the aryl-capped PLAs. These values were close to unity for the PLAs with a low index of association and showed a greater deviation from one with increasing end-group aggregation.

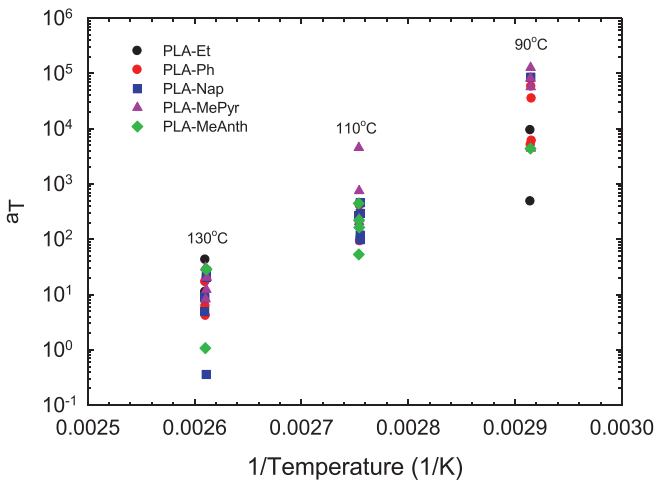

FIG. 1. The horizontal shift factors for all aryl-capped PLAs obtained from applying the time-temperature superposition principle.