

Report: Projekt week in the Samwer group

Dynamic Mechanical Analysis of *Poly(tert.-Butyl Acrylate-co-Acrylic Acid)* Copolymers Synthesized via Reversible Addition-Fragmentation Chain Transfer Polymerization

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Summary

During my project week I was actively involved in analyzing different samples of copolymers composed of *tert.*-butyl acrylate (*tBA*) and acrylic acid (*AA*) via dynamic mechanical analysis (*DMA*). The polymer samples were synthesized two weeks before during the project week of Moritz Schwabe in the group of Prof. Vana under my supervision.

Background

Copolymers of ethylene and (meth)acrylic acid have recently shown interesting relaxation behaviors depending on the distribution of the acid comonomer^[1]. Ethylene blocks of a new length scale, which are chemically confined via hydrogen bonds formed by the acid comonomer units, produce a new segmental motion.^[2-4] However, these copolymers are hard to tune with respect to molecular weight, polydispersity and distribution of the acid comonomer units. Therefore we decided to approach this field via Reversible Addition-Fragmentation Chain Transfer (*RAFT*) polymerization, which has become one of the most popular controlled radical polymerization techniques.^[5] Copolymers of *tBA* and *AA* were synthesized, which consist of an inner block composed of pure *tBA* and two outer blocks containing a statistical mixture of *tBA* and *AA*, hence enabling the formation of hydrogen bonds. The copolymers thus resemble an *ABA* block structure with the goal to observe an additional relaxation due to the flexibility of the *B* (pure *ptBA*) block.

Experimental

A Perkin-Elmer DMA 7 was used for the dynamic mechanical analysis in compression mode. Sample cylinders of 6 mm diameter and of 4 – 5 mm height were pressed and mounted in the DMA. A parallel quartz plate setup was used exerting a static uniaxial force of 600 mN superimposed by a dynamic force of 500 mN at a constant frequency of 1 Hz in case of the pure ptBA. In the case of the ABA block copolymers an uniaxial force of 500 mN was applied superimposed by a dynamic force of 400 mN at a constant frequency of 5 Hz. All measurements were executed in a nitrogen atmosphere with continuous removal of H₂O and O₂. Liquid N₂ cooling provided a vast temperature range from 130 – 140 K onwards.

Results

The project week produced preliminary results that are represented by two DMA measurements, one of pure ptBA and the other one of an ABA block copolymer sample. Both diagrams show that the samples become soft in the temperature range of about 270 – 280 K, where the $\tan \delta$ simultaneously increases. One can see that the sample positions decrease in this temperature range as well which further indicates a softening of the samples. In the case of the pure ptBA the $\tan \delta$ rises towards lower temperatures (below 200 K), which might suggest a γ -relaxation. However, in case of the ABA block copolymer sample, one can observe an additional maximum in the range between the two relaxations of the pure ptBA at 210 K. These three relaxations (called gamma, new and beta, see Figure 3) can be separated via gaussian fit functions which further suggest three different relaxation modes. However, systematic measurements, which are currently underway, are required to confirm the given observation.

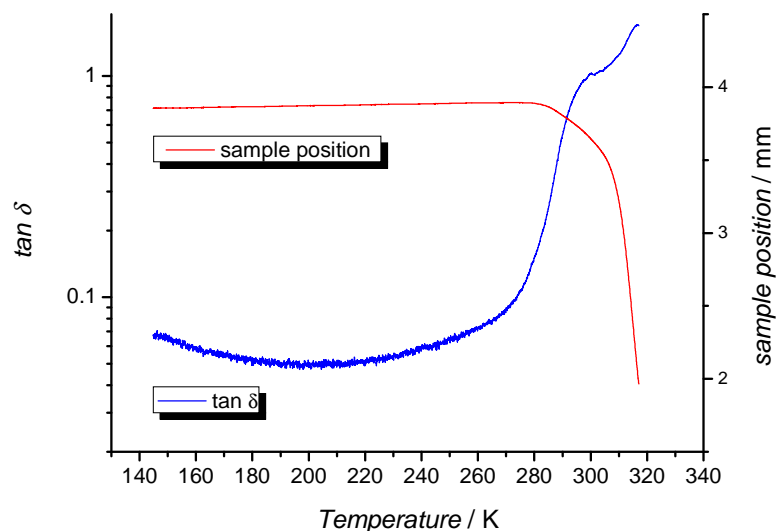


Figure 1. $\tan \delta$ and sample position of ptBA during DMA at a constant heating rate of $1 \text{ K} \cdot \text{min}^{-1}$ and a frequency of 1 Hz ($M_n = 39647 \text{ g} \cdot \text{mol}^{-1}$).

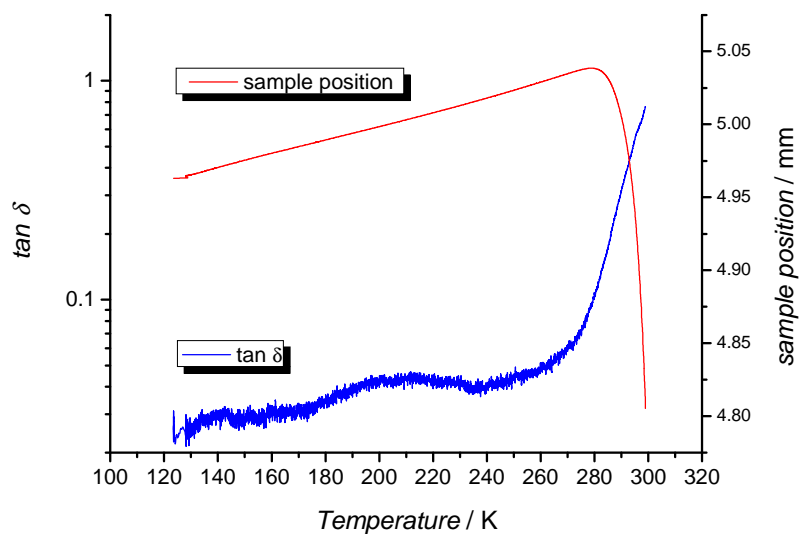


Figure 2. $\tan \delta$ and sample position of an ABA block copolymer sample during DMA at a constant heating rate of $1 \text{ K}\cdot\text{min}^{-1}$ and a frequency of 5 Hz ($M_n = 39647 \text{ g}\cdot\text{mol}^{-1}$, $M_n(\text{A}) = 12396 \text{ g}\cdot\text{mol}^{-1}$, $M_n(\text{B}) = 3472 \text{ g}\cdot\text{mol}^{-1}$).

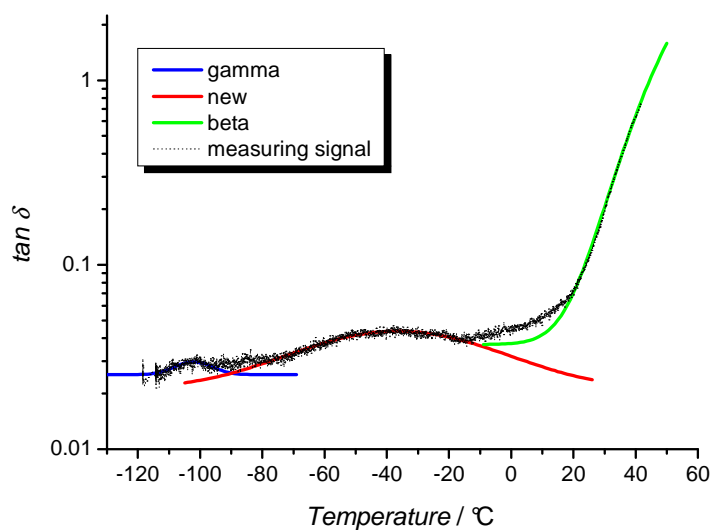


Figure 3. $\tan \delta$ and gaussian fits of possible relaxations of an ABA block copolymer sample during DMA at a constant heating rate of $1 \text{ K}\cdot\text{min}^{-1}$ and a frequency of 5 Hz ($M_n = 39647 \text{ g}\cdot\text{mol}^{-1}$, $M_n(\text{A}) = 12396 \text{ g}\cdot\text{mol}^{-1}$, $M_n(\text{B}) = 3472 \text{ g}\cdot\text{mol}^{-1}$).

Future Work

Various samples with distinct block lengths have to be analyzed in order to understand the origin of the observed relaxations and to assure reproducibility of the measurements. Samples of *pt*BA and of random copolymers of *t*BA and AA shall also be investigated as references in order to extract the relaxations that originate from the ABA block structure.

Acknowledgment

I would like to thank Prof. Samwer for giving me the opportunity to carry out my project week in his working group. My special thanks go to Moritz Schwabe for his very nice supervision.

References

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