Study on structure of polystyrene thin film

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Students per year: 80
Background

Study of properties like the glass transition temperature of polymer very thin films becomes more and more important as the manufactured devices get smaller.

The measure of the glass transition temperature \( T_g \) of a polymer, i.e. the transition temperature between its glassy state and its molten state, is a way to elucidate its structure.

It is known that the \( T_g \) of polymer films decreases for thickness below about 100nm. To explain that lowering, the widest believed hypothesis is the surface effect, however, it is not clearly proofed yet.

So the purpose of my research is to discuss that lowering from the point of view of the structure of thin films by changing and analyzing the effect of the conditions to make the thin film.
What the sample is?

- Solution of polystyrene in toluene
- $M_w \approx 400,000 \text{ g/mol}$
- $\approx 35 \text{ nm}$

How do I measure the thickness?

- Laser beam $\lambda = 636 \text{ nm}$
- Polarizer
- Analyser
- Sample
- CCD video camera
- Metal plate which temperature can be controlled

Spin coater

Thin film of polystyrene

We can change the thickness of the sample by changing the concentration and/or the rotation speed of the spin coater.

Ellipsometry

By analyzing the polarization state of the reflected beam we can deduce the thickness and the reflective index of the sample.

Assets: measures are very fast ($<0.1 \text{ s}$), easy to implement

Drawbacks: not accurate for some thickness, very sensible to the roughness and the homogeneity
How do I measure the glass temperature transition?

I measure the variation of the thickness with an increasing temperature. This variation depends on the structure of the film, so before and after $T_g$ the coefficient of thermal expansion changes. However the spin coating induces a very inhomogeneous structure and we can’t measure $T_g$ so we have to anneal the sample above $T_g$ for 1 min. ($T_g = 104^\circ C$ in bulk polystyrene).

Typical result after annealing

After annealing we can easily recognize two different states by the change of the coefficient of thermal expansion: the glassy state and the molten state. So we can deduce the $T_g$ of the sample: it is the intersection of the two lines.

$T_g = 89.2^\circ C$
Dependence of $T_g$ with the thickness and the concentration

Observations:

-the glass transition temperature decreases for concentration below 1 wt%.

-samples with the same thickness but different concentration don’t have the same value of $T_g$ for concentration below 1 wt%.

-the rotation speed doesn’t seem to have a so important effect on $T_g$. 
Discussion

Motion of the polymer molecules mainly affect $T_g$. Easier is the motion, lower is $T_g$.
For that molecular weight of polystyrene in toluene the overlapping concentration is about 0.8 wt%. So for concentration below this one the entanglement between molecules is far less important.

Thin film which concentration is above the overlapping concentration

A lot of entanglement
Motion is prevented
$T_g$ is near the bulk value

Thin film of same thickness which concentration is below the overlapping concentration

Few entanglement
Motion is easier
$T_g$ decreases

Therefore, according to the previous data, we may suppose that:
- the major factor which affect the value of $T_g$ is the concentration.
- the rotation speed, so the variation of thickness, is not the main factor.
Thank you very much for your attention.