

The Effect of the dn/dc parameter in Free Radical Polymerization using a Multifunctional Initiator

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Abstract – The variable dn/dc is used in GPC analysis and it is defined as the variation of the refractive index of a solution due to an increase in the concentration (g/ml). Works from literature and GPC instructions manual considered it a standard value for polystyrene. However, when a sample of polystyrene obtained using a trifunctional initiator was analyzed to calculate the dn/dc of this particular sample, the new value found was very different from the standard. So, the objective of this study is to explore the use of this new value in the analysis of GPC to verify changes in the values of molecular weights.

The variable dn/dc is used in GPC analysis. It is defined as the variation of the refractive index of a solution due to an increase in the concentration (g/ml) and it is always considered a standard value for polystyrene according to works from literature (Cerna et al., 2002 and Sheng et al., 2004, among others) and also to instructions manual of the equipment GPC. However, when a sample of polystyrene obtained with the initiator trifunctional is analyzed to calculate the dn/dc of this sample in particular, a very different value of dn/dc is found (Machado 2009). Using this new value of dn/dc , the molecular weights of all experiments were recalculated and the result was molecular weights higher than the previous values (values up to around 10^6). It should be noted that samples of polystyrene obtained with the trifunctional initiator, were much more rigid and more difficult to dissolve than samples of polystyrene obtained with mono- or bifunctional initiators. The experimental part consisted of the following procedures: purification of monomer, polymerization and characterization of the polymer. The synthesis of polystyrene was carried out using the method of polymerization in ampoules through a full range of conversion (Machado 2009). The polymer was characterized through analysis of molecular weight using the Gel Permeation Chromatography (GPC).

Figure 1 shows the differences between the values of molecular weights obtained with the dn/dc standard (linear PS) and the new dn/dc (TRI PS).

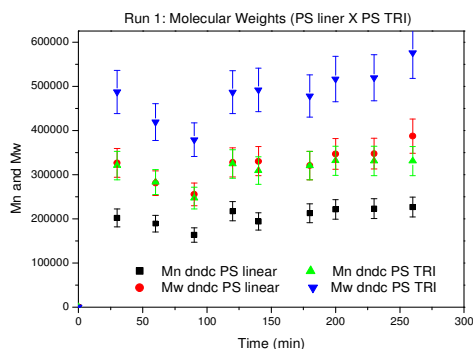


Figure 1: Pesos Moleculares, Mn e Mw X Tempo (PS TRI x PS padrão, Exp 1)

In Figure 1 it can be observed that the molecular weights obtained with the new value of dn/dc (PS TRI) are much higher than the ones obtained with the standard value (PS linear). The discovery of this new value of dn/dc was very interesting because it shows that polystyrene obtained by a trifunctional initiator probably has different structure, properties and characteristics from polystyrene obtained by mono- or bifunctional initiators. This approach should be always considered, since the results obtained with the adjustment of the dn/dc are more realistic, because they provide higher values of molecular weights, consistent with the rigidity found in the samples of polymers obtained from a trifunctional initiator.

References

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