GPC analysis of PE and PP: absolute calibration via quenched-flow polymerization methods in combination with high-temperature cryoprobe NMR measurements.

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High-temperature GPC is probably the most widely used method to asses average molecular weights (MWs) and molecular weight distribution (MWD) of polyethylene (PE) and polypropylene (PP) based materials. Typically, universal calibration based on monodisperse polystyrene standards is adopted, which is easy to do but conceptually questionable. As a matter of fact, the thus determined relative GPC values of M_n and M_w may differ appreciably from absolute values measured e.g. by NMR. In alternative, well-defined PE and PP samples usable as GPC calibration standards can be prepared by transition-metal-mediated polymerization under 'controlled' kinetics. When the controlled regime is inherent to the catalyst, MWD values between 1.0 and 2.0 are obtained. On the other hand, quenched-flow methods can be adopted to 'force' any coordination catalyst to operate under controlled conditions; this includes heterogeneous multi-sited systems, yielding much broader MWDs. In this presentation, the absolute M_n and M_w values of PE and PP samples made in a quenched-flow reactor at variable MWD, measured precisely by means of NMR spectroscopy with high-temperature cryoprobe technology, are compared systematically with relative GPC values obtained using universal calibration. The differences will be highlighted and some trends will be commented.

References:

1. Taniike, T.; Sano, S.; Ikeya, M.; Thang, V. Q.; Terano, M. *Macromol React Eng* **2012**, 6, 275.
2. Zhou, Z; Kümmerle, R.; Stevens, J. C.; Redwine, D.; He, Y.; Qiu, X.; Cong, R.; Klosin, J.; Montañez, N.; Roof, G. *J Magn Reson* **2009**, 200, 328.
3. Busico, V.; Cipullo, R. *Prog Polym Sci* **2001**, 26, 443.
4. Paynter, O. I.; Simmonds, D. J.; Whiting, M. C. *J Chem Soc, Chem Commun* **1982**, 1165.
5. Wu, Z.; Grubbs, R. H. *Macromolecules* **1994**,27, 6700.
6. Makio, H.; Terao, H.; Iwashita, A.; Fujita, T. *Chem Rev* **2011**,111, 2363.
7. Tian, J.; Hustad, P. D.; Coates, G. W. *J Am Chem Soc* **2001**, 123, 5134.