AN EVALUATION OF DILUTION RHEOLOGY FOR THE CHARACTERIZATION OF LONG CHAIN BRANCHING OF POLYETHYLENES

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ABSTRACT:
The purpose of this paper was to re-evaluate the novel rheological method of Crosby et al. [J. Rheol. 46 (2002) 401] to characterise long chain branching (LCB) in polyethylenes (PE) using the rheology of concentrated solutions. The feasibility of this dilution method centred on knowing the class of branched material and the molecular tube theory-based technique for the determination of two topological parameters (n, b^U), where n is the number of entanglements between branch points while b^U is the probability of meeting a branch point when tracing along the molecule from a random monomer against the direction of polymerisation. This paper proposes new possible approaches to calculate the two topological parameters (n, b^U) set for metallocene polyethylenes (mPE), and their ambiguity discussed, as the results are dependent on the approach taken, though the previous authors mentioned only one. In addition, their approach requires an input value of LCB/1000C obtained from the standard analytical solution (SEC-V or SEC-LALLS) methods, hence, until now, without proper demonstration of the potential advantage of the dilution rheology method for LCB characterisation, as the main premise of their published article was to characterise the degree of LCB via rheological measurements without recourse to other methods of LCB characterisation.

ZUSAMMENFASSUNG:
Das Ziel dieses Artikels war die neue rheologische Methode von Crosby et al. [J. Rheol. 46 (2002) 401] zu evaluieren, um die Langkettenverzweigung (LCB) in Polyethylenen mit Hilfe der Rheologie von konzentrierten Lösungen zu charakterisieren. Die Eignung dieser Verdünnungsmethode basierte auf der Kenntnis der Klasse von verzweigten Materialien und der Technik zur Bestimmmung der beiden topologischen Parameter (n,b^U), die auf der molekularen Röhrentheorie basieren, wobei n die Anzahl der Verschlaufungen zwischen zwei Verzweigungspunkten ist und b^U die Wahrscheinlichkeit ist, einen Verzweigungspunkt auf dem Pfad entlang des Moleküls von einem zufälligen Monomer in Richtung der Polymerisation zu treffen. Dieser Artikel schlägt neue mögliche Ansätze vor, um die beiden topologischen Parameter (n,b^U) für Metallocen-Polyethylene (mPE) zu berechnen, und die Mehrdeutigkeit wird diskutiert, da die Resultate unabhängig vom Ansatz sind, obwohl die früheren Autoren nur ein Resultat erwähnen. Darüber hinaus erfordert ihr Ansatz einen Eingabewert für LCB/1000C, der mit der herkömmlichen Standardlösungsmethode (SEC-V oder SEC-LALLS) erhalten wird ohne einer geeigneten Demonstration des Vorteils der Lösungsrheologiemethode für die LCB-Charakterisierung. Die wesentliche Voraussetzung ihres publizierten Artikels war die Charakterisierung des LCB-Grades durch rheologische Messungen ohne Vergleich mit anderen Methoden der LCB-Charakterisierung.

RÉSUMÉ:
L'objet de cet article est de re-évaluer la nouvelle méthode rhéologique de Crosby et al. [J. Rheol. 46 (2002) 401] afin de caractériser le branchement de grandes chaînes dans les polyéthylènes (PE) en utilisant la rhéologie de solutions concentrées. La faisabilité de cette méthode de dilution est axée sur la connaissance de la classe de matériaux branchés et de la technique théoriquement fondée de tube moléculaire pour la détermination de 2 paramètres topologiques n et b^U, ou n est le nombre d'enchevêtrements entre les points de branchement, tandis que b^U est la probabilité de rencontrer un point de branchement en parcourant la molécule à partir d'un monomère aléatoire. Cet article propose de nouvelles approches possibles pour calculer les 2 paramètres topologiques pour des polyéthylènes métalocènes (mPE). Leur ambiguïté est également discutée puisque les résultats dépendent de l'approche entreprise, même si les auteurs précédents n'en n'ont mentionnée seulement qu'une. De surplus, leur approche requiert l'introduction d'une valeur de LBC/1000C obtenue à partir des méthodes standards d'analyse de solution (SEC-V ou SEC-LALLS), et donc, jusqu'à présent, sans une démonstration convenable de l'avantage potentiel de la méthode de rhéologie de dilution pour la caractérisation de LCB, puisque la principale idée de leur article publié était de caractériser le degré de LCB via des mesures rhéologiques sans recourir à d'autres méthodes de caractérisation de LCB.

KEY WORDS: Polyethylene, long chain branching, rheology, polymer, metallocene, molecular topology

5 CONCLUSION

For the method of dilute rheology, there appears to have 3 different approaches to calculate the (n, b^U) parameter set for characterising the topological structure of long-chain-branched metallocene polymers, where the results were found to be dependent on the approach taken.

- The initial method [16], classified as Approach (a), requires the value of LCB/1000C obtained from the solution method. If one were to use the value of LCB/1000C predetermined from SEC-LALLS, this would render the dilution method redundant, as the main premise of the previously published article was to characterise the degree of LCB via rheological measurements without recourse to other methods of LCB characterisation.
- As for the Approach (b), it requires only two independently measured input values, rather three for Approach (a), to determine (n, b^U). This approach inherits relatively least errors and does not require any recourse to other LCB characterisation techniques. In our work, we have used Approach (b) to evaluate the degree of LCB of a new set of polymers. The LCB ranking of these polymers is in agreement with that based on GPC-V measurements and the ratio of M_b/M_c based on Janzen and Colby [12]. This could suggest the validity of this approach.

We have confirmed in our study that the dilution-rheology method is indeed sensitive to the presence of LCB, as it was thus claimed [16]. It gives a clear signal revealing its presence. However, one should note the limit of the dilution theory. If we have a linear polymer, the predicted gradient from Eq. 5 will be null (since $\phi_b = 0$). In other words, the theory predicts no variation in the relaxation times, which contradicts with the physical observations.

The idea of this dilution rheology method is not far from that of SEC-V. Both methods involve the dilution of polymer in order to have intrinsic information of a chain. The latter quantifies the LCB via the hydrodynamic volume whereas the former via the number of entanglements per chain or the average molecular weight between branch points. One major drawback of this dilution rheology method is its time-consuming sample preparation step. In addition, this method still requires an independent measure of M_W from SEC, as well as the knowledge of the type/topology of LCB present in the polymer, to quantify the LCB. Hence, dilution-rheology measurements alone are not sufficient for the quantification of the degree of LCB present in PE. However, theoretically, we can make the dilution rheology method independent simply by measuring the gradient, if and only if, we have two polymers of identical LCB type and molecular weight (doubtless, we would need SEC measurements for this purpose but not for the ranking of LCB). In this particular case, the gradient itself depends solely on the degree of LCB. This method does provide important insights into the topology of polymer.

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