Optimal Descriptor Based QSPR Models for Catalytic Activity of Propylene Polymerization

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ABSTRACT

A heterogeneous Ziegler–Natta (ZN) catalyst is an important catalyst in the field of the polypropylene polymerization industry. The role of electron donors has been crucial in the ZN catalyzed polypropylene polymerization process. In this article, quasi-SMILES-based QSPR models are elaborated for the prediction of catalytic activities. The representations of the molecular structure by quasi-simplified molecular input line entry system were the basis to build the desired QSPR model. These models were developed by means of the Monte Carlo optimization involving the available methods classic scheme (CS), balance of correlations (BC) and balance of correlation with ideal slopes (BCIS). The best QSPR model showed $r^2 = 0.813$ (for external validation set), $r_m^2 = 0.73$ and $\Delta r_m^2 = 0.03$.

KEYWORDS

Optimal Descriptor, Propylene Polymerization, Quantitative Structure–Property Relationship, Quasi-SMILES

1. INTRODUCTION

Ziegler-Natta polymerization is an important method for vinyl polymerization, as it provides control to prepare the polymers of specific tacticity. The preparation of the linear unbranched polyethylene and isotactic polypropylene is only possible by Ziegler-Natta catalysts. Today in the manufacture of polypropylene (PP), most of the commercial catalysts are obtained by modifying the parent Ziegler–Natta system (Ratanasak, Rungrothmongkol, Saengsawang, Hannongbua, & Parasuk, 2015; Taniike & Terano, 2012). These catalysts comprise the MgCl$_2$ supported TiCl$_4$ catalyst in conjunction with triethylaluminium [Al(C$_2$H$_5$)$_3$] as co-catalyst and organic additives (electron donors) for the production of isotactic polypropylene. These electron donors can be internal donors (which are added during the catalyst preparation) or external donors for the propylene polymerization process (Ratanasak et al., 2015). Internal electron donors are bonded directly to the MgCl$_2$ support and activate the site formation whereas the external electron donor could selectively poison these sites (Albizzati et al., 1995; Xu, Feng, & Yang, 1997; Makwana et al., 2009; Matyjaszewski, Gaynor, Greszta, Mardare, & Shigemoto, 1995; Sacchi, Tritto, & Locatelli, 1991). Therefore, the direct relation of these internal donors such as phthalates, 1,3-diethers and malonates present in ZN catalyst with the production of the polypropylene is obvious and interesting. The polypropylene activity (PP$_{act}$) can be defined as the how many kilograms of PP are obtained per gram of the ZN catalyst with 29 internal electron donors: Phthalates, 1, 3-diethers and Malonates. The PP$_{act}$ is expressed in kg PP/g Cat. Earlier attempts have been made to correlate PP$_{act}$ with adsorption energy (Ratanasak et al., 2015); however, the correlation between the PP$_{act}$ and the internal donors of ZN catalyst is so far not reported in detail.

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We know that the quantitative structure activity/property relationship (QSAR/QSPR) is a proven technique to predict the desired activities/properties from the molecular properties. The QSAR/QSPR is also successfully applied for both homogenous (Cruz et al., 2004; Cruz, Martinez, Martinez-Salazar, Polo-Cerón, et al., 2007; Cruz, Martinez, Martinez-Salazar, Ramos, et al., 2007; Martínez, Cruz, Ramos, & Martínez-Salazar, 2012; Yao, Shoji, Iwamoto, & Kamei, 1999) and heterogeneous catalysts (Cruz, Martinez, Martinez-Salazar, Polo-Cerón, et al., 2007; Fayet, Raybaud, Touhoat, & de Bruin, 2009; Tognetti, Fayet, & Adamo, 2010). This field helps in designing materials, screening of potential catalysts before the material being synthesised minimizing the cost and sometimes can suggest the mechanism (Boudene, De Bruin, Touhoat, & Raybaud, 2012; Colosi, Huang, & Weber, 2010; di Lena et al., 2010; Manz et al., 2012; Taniike & Terano, 2012; Wu et al., 2012). Also, good QSAR models could be built by known paradigms such as "Endpoint = f (SMILES)" (Achary, 2014; Begum & Achary, 2015), "Endpoint = f (quasi-SMILES)". The quasi-SMIES, the representation of eclectic data, can be symbols of the SMILES structure/or groups in the molecular structure. (Toropov et al., 2013; Toropov & Toropova, 2014; Toropova & Toropov, 2013).

In the present report, attempts have been made to build QSPR models between polypropylene activity (PP$_{act}$) (kg PP/g Cat.) and optimal descriptors obtained from the quasi-SMILES codes of 29 internal electron donors, phthalates, 1,3-diethers and malonates.

2. METHODS

2.1. Data

The dataset for the polypropylene activity (kg PP/g Cat.) of 29 internal electron donors: phthalates, 1, 3-diethers and malonates is obtained from the literature (Ratanasak et al., 2015). The details about the quasi-SMILES code for the molecules is described in our previous publication regarding the prediction about adsorption energy (kcal/mol) (Achary, Begum, Toropova, & Toropov, 2016). The quasi-codes and the respective polypropylene activity (PP$_{act}$) (kg PP/g Cat.) is listed in the Table 1. The interpretation of the different quasi-SMILES codes are listed in Table 2.

2.2. Descriptors and Methods of Monte Carlo Optimization

The CORAL software (Coral 1.5, 2010; available at http://www.insilico.eu/coral) is used for the Monte Carlo Optimization. The quasi-SMILES-based optimal descriptors (Xu et al., 1997; Toropov, Toropova, & Benfenati, 2010; Toropova et al., 2010) were calculated as per the following equation

$$DCW(T,N) = \sum CW(S_i)$$ (1)

where $S_i$ are the quasi-SMILES attributes extracted from quasi-SMILES and CW ($S_i$) is correlation weight for each $S_i$. The Monte Carlo optimization process to build a QSPR model requires a good number of epochs to maximize a given target function. The available functions in CORAL are (i) The classic scheme (CS), i.e., [training test, without calibration set] system; (ii) balance of correlations (BC), i.e., [sub-training set, calibration set and test set] system; and (iii) balance of correlations with ideal slopes (BCIS). The involved optimization process is well documented in the literature (Toropova et al., 2010; Toropova et al., 2011).

The building of a good predictability QSAR/QSPR model with greater accuracy and precision needs two prime factors: Threshold T and N$_{epoch}$ (Toropov et al., 2010; Toropova et al., 2010). The effect or influence of the two parameters in predicting the PP$_{act}$ could be ascertained by the correlation coefficients ($r$) between experimental and predicted values for the training set, calibration set and validation set. The validation and robustness of these models are further verified by a set of eight internal donors which are not used in building the models, are treated as ‘invisible validation set.’
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