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Theoretical Investigation and Quantum Chemical QSPR Study of The Best Parameters Influences on Glass Transition Temperatures of polymer Compounds.

دراسة نظرية وكمية بتقنيات QSPR لأفضل تأثير للمتغيرات على درجة الانتقال الزجاجي للمركبات البوليمرية

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Abstract

The glass transition temperatures (Tg^oc) of polymer understudy are described by a quantitative structure- property relationship QSPR. The QSPR model has been derived from a set of 6 polymer compounds to correlate and predict their glass transition temperatures (Tg^oc). It consists of seven equations with six descriptors calculated from the molecular structures with quantum chemical methods. The best results are obtained seven equations with a group of QSPR models with three and four structural descriptors, with the best a correlation coefficient (three descriptor) R^2=0.994 (eq 7), (four descriptor) R^2=0.998(eq 5) respectively. For all results the best QSPR models show excellent model by Eq 5. Which depends on four descriptors with highs of R^2, F, and minimum S by using four descriptors [nC, nO, VOLUME and S. A], was found and indicate that these parameters have an important role in determining the properties of glass Transition Temperatures (Tg^oc). This result of quantum-chemical descriptors show the applicability of molecular orbital calculations in deriving useful descriptors, by obtaining highly significant correlations described quantitatively by equations with just three or four solely theoretical molecular descriptors. Finally, the most promising of a computational modeling approach can significantly reduce the costs and labor associated with identifying high-performance for specific applications

Keywords. Polymer, Glass Transition Temperature, QSPR Model.

الخلاصة:

درجة الانتقال الزجاجي للبوليمرات المدروسة وصفت باستخدام تقنيات QSPR . الدراسة تضمنت العلاقة التركيبة ل 6 من المركبات البوليمرية لايجاد العلاقة التركيبية والتنبأ بقيم درجة الانتقال الزجاجي للمركبات بأستخدام سبعة معادلات مع ستة متغيرات والتي تم حسابها من الخواص التركيبية والجزيئية وباستخدام طرق كيمياء الكم .افضل النتائج لموديلات المعادلات السبعة اعتمدت على ثلاثة واربعة متغيرات مع قيم عالية ل (R^2=0.994 (eq 7 ثلاث متغيرات) و (R^2=0.998(eq 5 اربعة متغيرات). وبين كل الموديلات افضل النتائج كان الموديل الممتاز هو معادلة 5 والذي اعتمد على اربعة متغيرات [nC, nO,VOLUME and S. A] مع قيم عالية R^2, F واقل قيمه ل S .والتي اثبتت بأن هذه المتغيرات لها اهمية كبيرة في تحديد خواص درجة الانتقال الزجاجي للبوليمرات المدروسة ..وهذه نتائج تشجع لدراسة وتطبيق تقنيات QSPR لمدى اوسع من الخواص البوليمرية وانواع اخرى من البوليمرات .

Introduction

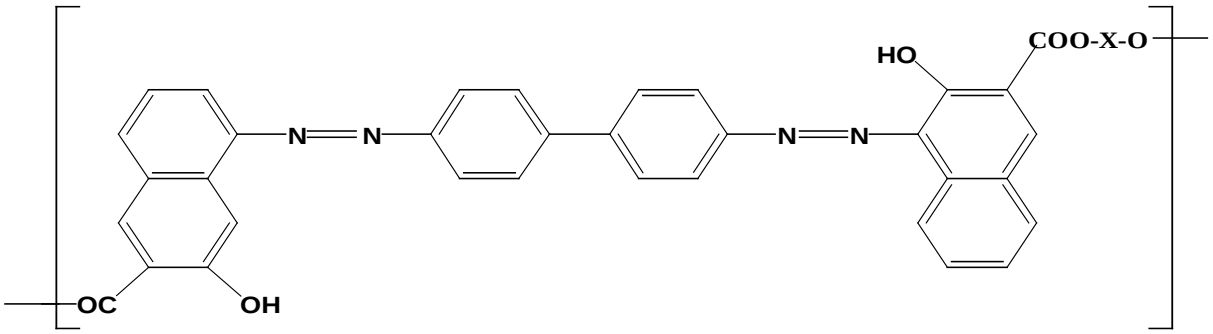
Polymers exhibit various physical and mechanical behaviors, depending on the temperature. At low temperatures, polymers are glassy, hard, and brittle. As the temperature is increased, however, they undergo a phase transition, known as the glass rubber transition(the glass transition (Tg^oc)), which is accompanied by drastic changes in their properties. The glass transition is the most important thermal transition that a polymer undergoes.[1] Therefore, the study of (Tg^oc) is very important for the polymeric material which used in many applications . Prediction of physical properties of polymers gained a great interest in actual period because of its utility of provided

information about structural design of polymers and, on the other hand, because of no experimental difficulties required, except for software programs and theoretical databases [2–4]. The search for regularities in the manner in which various molecular properties change, depending upon their molecular structures, is the main subject of investigations in this field (QSAR/QSPR). In this way, QSAR/QSPR investigations have opened a new page in the history of computer applications in chemistry and created extensive software dealing with the search for structure-activity/property relationships during the past 2 decades. The major goal of any QSAR/QSPR research is to assign to the structure a number or a set of numbers which (i) must correlate well with the property (activity) value measured experimentally and, if possible, (ii) should provide some physical insight to the molecular behavior[5-8]. In QSPR/QSAR analysis, there were many properties that could be studied [9-12].

In this paper a theoretical technique has been discussed by which the glass transition temperature (Tg^oc) of polymer compounds can be measured prior [13] . The goal of this paper is to produce a robust QSPR model that could predict (Tg^oc)values for 6 polyesters using quantum chemical descriptors, which are calculated from the monomers of polyester with ortho-hydroxyazo groups.

Modeling and Geometry Optimization

Theoretical calculations were performed on hyperchem program version 7.5[14], running on a Pentium V PC-CPU 3400GHz. The volume and surface area obtained from QSAR properties in hyperchem 7.5 , while vander wales calculated by facio version 14.2.4 [15]. The experimental glass transition temperature (Tg^oc) data of 6 compounds under study has been taken from reference [13] The structures of these compounds are shown in Figure.1



Repeating unit of polymer understudy

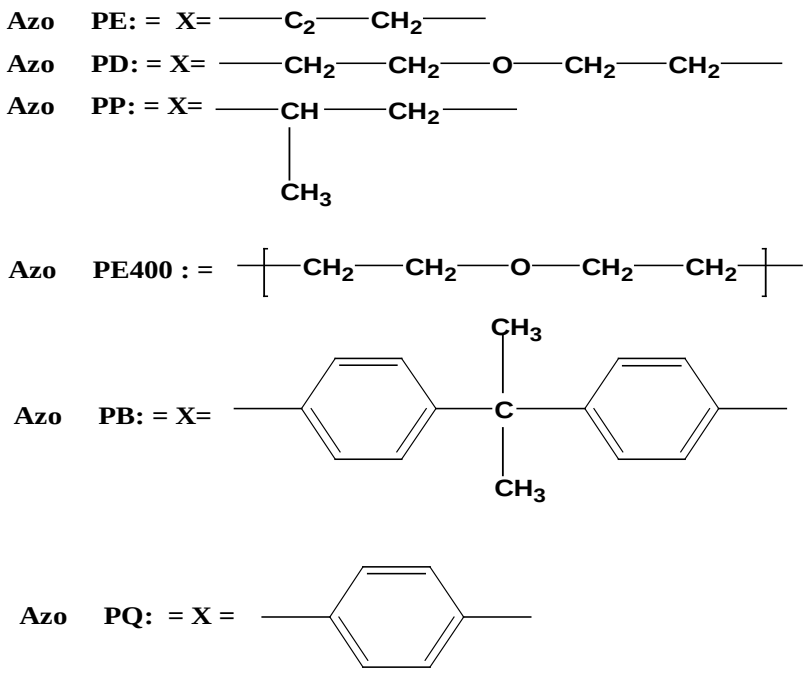


Figure 1. Molecular structure of compounds used in the present study.

Results and Discussion

In order to build QSPR model. The establishment a mathematical model connecting the experimental temperatures characteristic of glass transition temperatures (Tg^oc) to values obtained by quantum study of proposed descriptors (QSPR). The QSPR mathematical models consist of multiple regressions taking into account only the influential descriptors. Using the linear model, multiple linear regressions (MLR) were performed between glass transition temperatures (Tg^oc) of polymer and some quantum chemical parameters/descriptors. Regarding the polymer compounds understudy, the computation model was established based on its structural unit that the terminal causes its integrity with the hydrogen seal[16-19].

In a QSPR study, generally, the quality of a model is expressed by its fitting ability and prediction ability, and of these the prediction ability is the more important. The prediction set, consisted of six molecules, was used to evaluate the generated model. It is clear that many (MLR)models will result using the stepwise multiple regression procedure; among them we have to choose the best one. It is common to consider five statistical parameters for this purpose. These parameters are the number of descriptors, correlation coefficient (R^2) for training and prediction sets, standard error (SE) for training and prediction sets and F statistic. A reliable MLR model is one that has high R^2, and F values, low SE and least number of descriptors[20-23]. In addition to these, the model should have a high predictive ability. The descriptors, which were significant for experimental data, were selected by a QSPR - contingency module which calculated shown in table 1.

Table 1. Recapitulation of descriptors as the independent variables used for QSPR analysis of polymers .

Name	nC	nO	V.WV	S. A	Volume	Exp Tg^oc
PB	50	7	697.717	956.67	2103.95	78.44
PD	39	8	580.973	888.97	1801.45	69.96
PE	37	7	537.619	782.37	1661.77	76.07
PP	38	7	925.765	1296.73	2679.32	65.21
PE400	55	16	554.673	808.96	1707.9	89.53
PQ	41	7	574.941	797.14	1763.21	82.26

Definition of Descriptors Used in This Study.

nC = Number of carbon atoms in repeating unite, **nO =** Number of oxgen atoms in repeating unite, **v.w v =** VANDER WALES Volume in A^3 according the Facio program version 14.2.4.[15]., **S. A**= surface area, **Volume** =in A^3 .

The number of equations depends on (two, three and four descriptors) were generated by using all the variables, which is as follows:

four descriptors: Equations 1,2, 3, 4 and 5. Depends on four descriptors. The model which depends on only four descriptors [nC, nO, V.W.V and VOLUME] gave good model with correlation coefficient R^2 values for this model of 0.972, as equation 1. The suggest that the glass transition temperatures (Tg^oc) increases with increase values of this descriptor.

Tg =1.0768 nC-0.7551nO+0.7930 V.W.V-0.3162 VOLUME+142.6069**…….Eq 1.**

Statistical characteristics of the obtained model equation :

n =6 R^2= 0.972 F=8.927 S=3.200

According to this equation, these descriptors [nC, nO, V.W.V and VOLUME] have a major rule and has a positive value to predict transition temperatures (Tg^oc). The relationship between the experimental data and predicted glass Transition Temperatures (Tg^oc) shown in Fig.2**.**

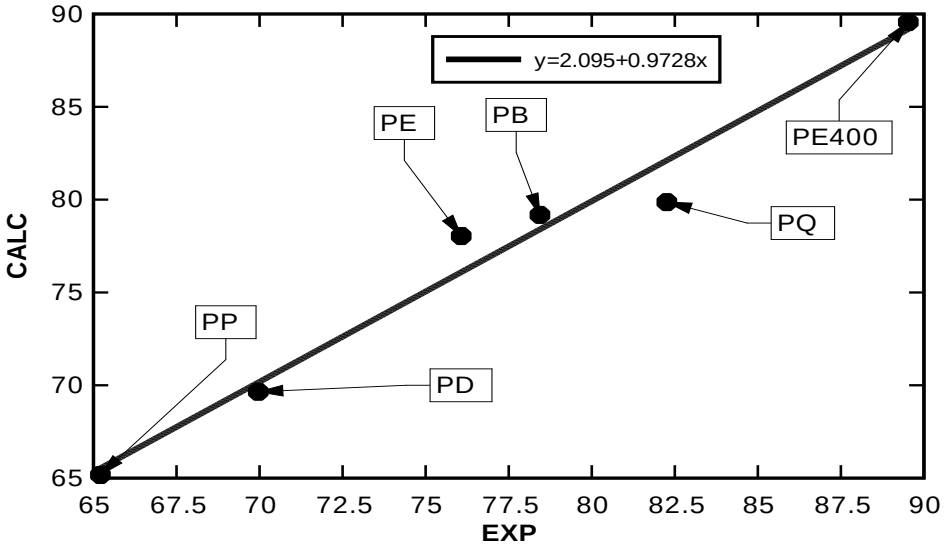


Fig. 2. Plot of the experimental (Tg^{o}c) vs. calculated (Tg^{o}c) of polymers using Eq 1.

In equation 2, which contain the four descriptors [nC, VOLUME, V.W.V and S. A]give good model with correlation coefficient R^2 values 0.983. by replacing the descriptor [nO]in eq 1, by the descriptor [S. A].

Tg =0.7106 nC-0.1975VOLUME+0.5643V.W.V-0.0608S.A+123.8932**…….Eq 2.**

Statistical characteristics of the obtained model equation :
n =6 R^2= 0.983 F=14.902 S=2.491
The relationship between the experimental data and predicted glass Transition Temperatures (Tg^{o}c) shown in Fig.3**.**

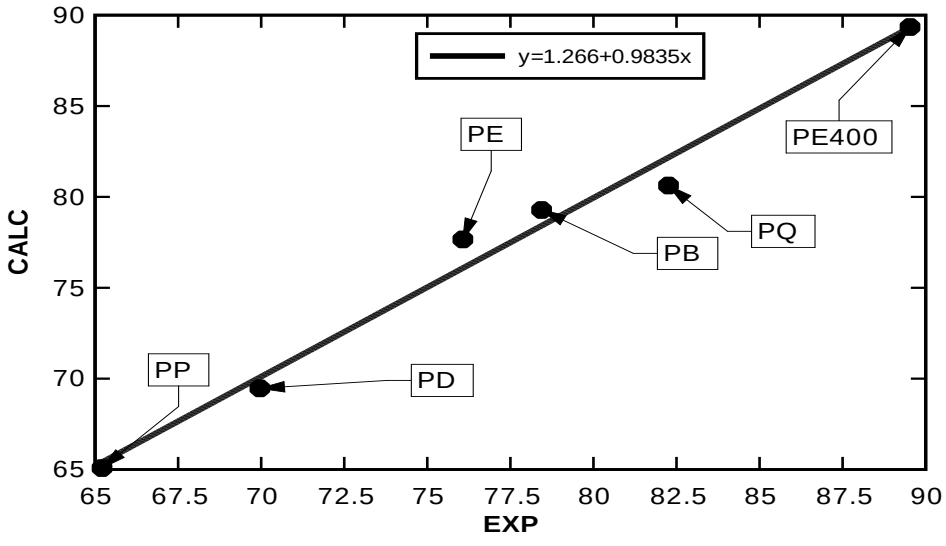


Fig. 3. Plot of the experimental (Tg^{o}c) vs. calculated (Tg^{o}c) of polymers using Eq 2.

While when replacement the descriptor [VOLUME] in equation 2, by[nO] in equation 3, this equation become depends on the four descriptors [nC, nO, V.W.V and S. A]. In this equation 3, note a slight improvement in the value of the correlation coefficient R^2 = 0.995. in comparison with eq 2**.**

Tg =5.5602E-02nC+1.4150 nO+0.1748V.W.V-0.1549S.A+92.1911**…….Eq 3.**
Statistical characteristics of the obtained model equation :
n =6 R^2= 0.995 F=54.503 S=1.310
The relationship between the experimental data and predicted glass Transition Temperatures (Tg^oc) shown in Fig.4**.**

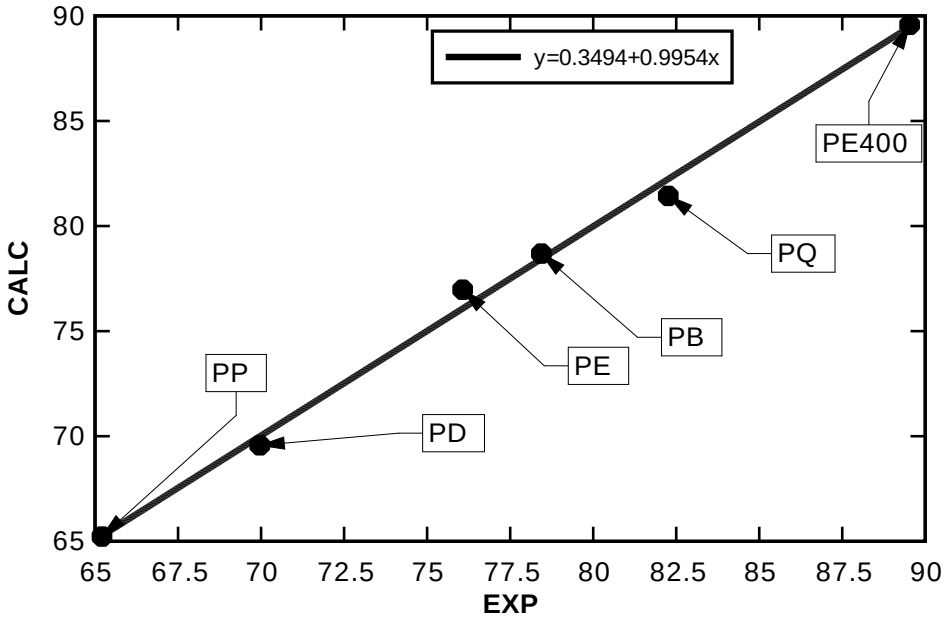


Fig. 4. Plot of the experimental (Tg^oc) vs. calculated (Tg^oc) of polymers using Eq 3.

In equation 4, the descriptors which using to generate equation 4, was [VOLUME, nO, V.W.V and S. A].by replacement descriptor [nC] in eq 3, by the descriptor[VOLUME] in eq 4. This lead to a simple increase in the value of the correlation coefficient R^2 = 0.996 .

Tg =2.9979E-02 VOLUME+1.5473nO+0.1092V.W.V-0.1643S.A+85.9363**…….Eq 4.**

Statistical characteristics of the obtained model equation :
n =6 R^2= 0.996 F=68.1018 S=1.172
The relationship between the experimental data and predicted glass Transition Temperatures (Tg^oc) shown in Fig.5**.**

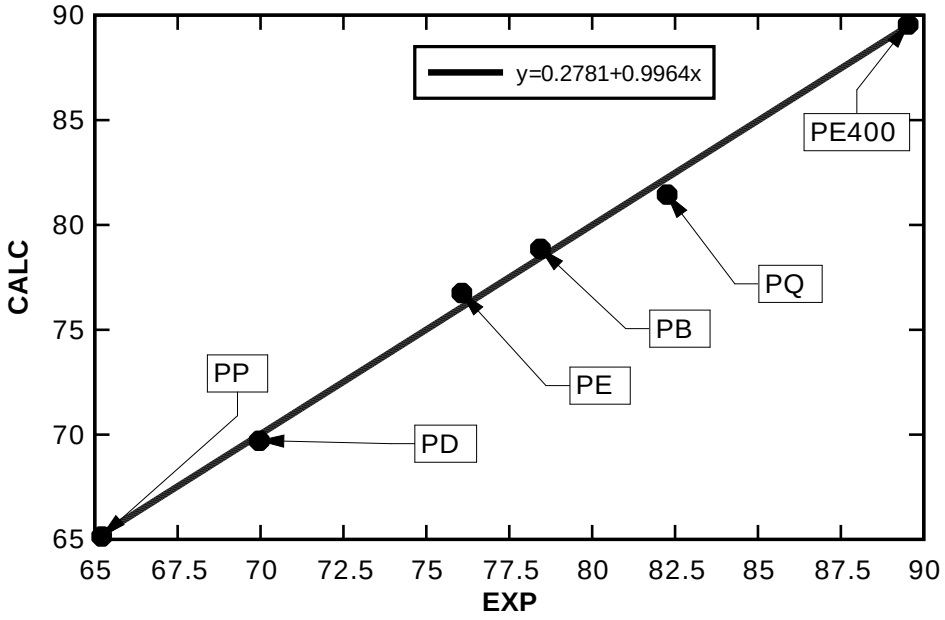


Fig. 5. Plot of the experimental (Tg°c) vs. calculated (Tg°c) of polymers using Eq 4.

But when replace the descriptor[V.W.V] in equation 4, by using the descriptor (nC) to configure the equation 5.this model depends on the descriptors [nC, nO, VOLUME and S. A]and we see significant change and increase in the value of the correlation coefficient R^2 become 0.998,low standard error and the highest of the sequential Fischer test(F), in contrast with equations1,2,3 and 4. .

Tg =-0.2125nC+1.9876nO+8.7310E-02VOLUME-0.1944S.A+77.6688**…….Eq 5.**

Statistical characteristics of the obtained model equation :

n =6 R^2= 0.998 F= 140.096 S=0.8185

The relationship between the experimental data and predicted glass Transition Temperatures (Tg^oc) shown in Fig.6**.**

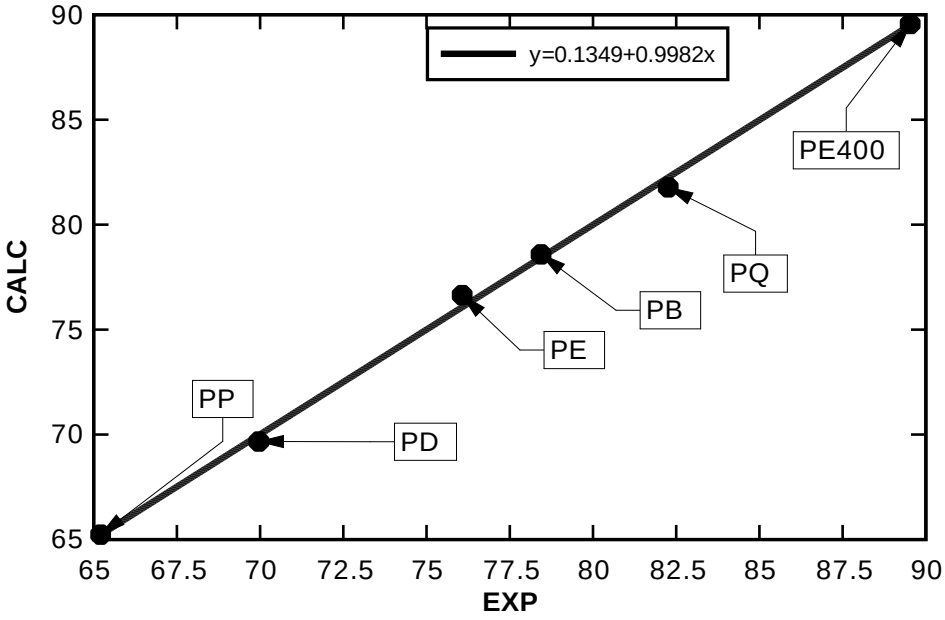


Fig. 6. Plot of the experimental (Tg°c) vs. calculated (Tg°c) of polymers using Eq 5.

Three descriptors: the best two model when depend on only two descriptors eq 6 and eq 7. The correlation coefficient R^2 of eq 6., when included the [nO**,** S. A and VOLUME] obtained very good model with correlation coefficient R^2 values for this model of 0.993, as equation 6.

Tg =1.5915nO-0.1664S.A+7.2929E-02 VOLUME+74.1214**…….Eq 6.**

Statistical characteristics of the obtained model equation :
n =6 R^2= 0.993 F=99.235 S=1.120

The relationship between the experimental data and predicted glass Transition Temperatures (Tg^oc) shown in Fig.7**.**

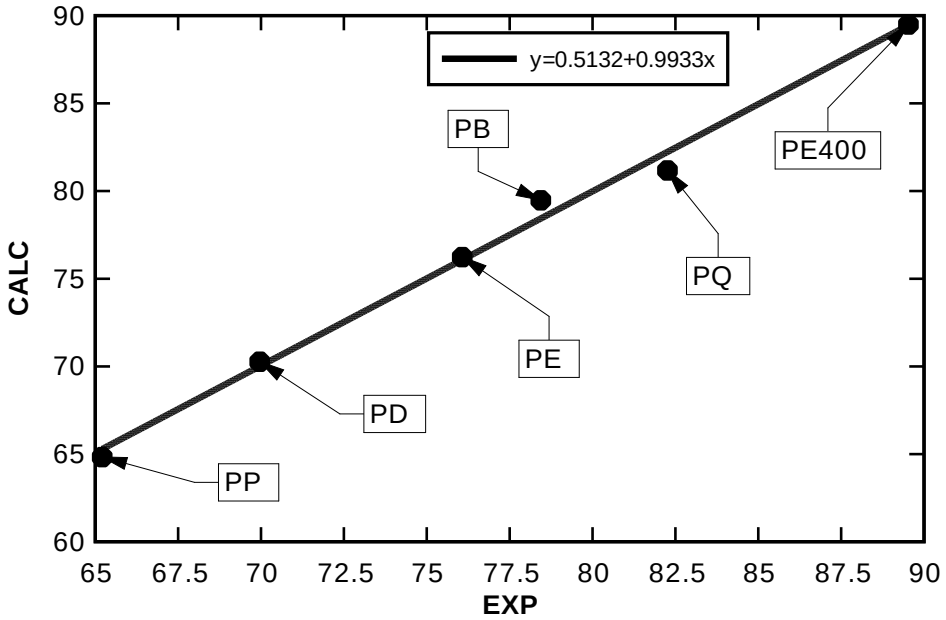


Fig. 7. Plot of the experimental (Tg^oc) vs. calculated (Tg^oc) of polymers using Eq 6.

The second best equation was Eq 7. Included this descriptors [V.W.V**,** S. A and nO] gave excellent model with correlation coefficient R^2 values for this model of 0.994, as equation 3. When replacement the descriptor [VOLUME] in eq 6., by the descriptor [V. W. V].

Tg =0.1828V.W.V-0.1608 S.A+1.5124nO+94.1145**…….Eq 7.**

Statistical characteristics of the obtained model equation :
n =6 R^2= 0.994 F=130.692 S=0.976
The relationship between the experimental data and predicted glass Transition Temperatures (Tg^oc)shown in Fig.8**.**

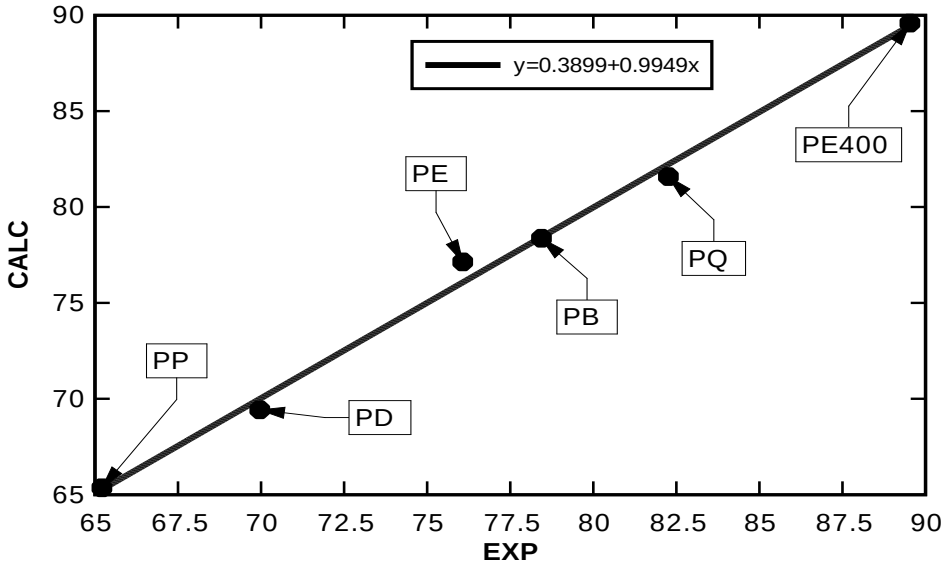


Fig. 8. Plot of the experimental (Tg°c) vs. calculated (Tg°c) of polymers using Eq 7.

Sevene equations with one, two, three and four descriptors were modeled in which R^2 value increases with increasing numbers of the descriptors. These descriptors as following in Table 1, which used to build up the predictive model of QSPR study[22]. In the formation of the predictive model with employ all variables and the best-fitted equations of the models to predictive the glass transition temperatures (Tg^oc)of polymer shown in Table 2.

Table 2. Values of descriptors plus experimental and predicted values of (Tg^oc) for Each of the six polymers used in the study.

Name	*Exp	Calc by eq 1	Calc by eq 2	Calc by eq 3	Calc by eq 4	Calc by eq 5	Calc by eq 6	Calc by eq 7
PB	**78.44**	**79.179**	**79.2811**	**78.692**	**78.86**	**78.586**	**79.469**	**78.37**
PD	**69.96**	**69.65**	**69.469**	**69.568**	**69.707**	**69.667**	**70.26**	**69.426**
PE	**76.07**	**78.039**	**77.6631**	**76.973**	**76.754**	**76.642**	**76.23**	**77.137**
PP	**65.21**	**65.1681**	**65.082**	**65.226**	**65.141**	**65.232**	**64.83**	**65.36**
PE400	**89.53**	**89.564**	**89.3471**	**89.573**	**89.558**	**89.562**	**89.495**	**89.589**
PQ	**82.26**	**79.868**	**80.626**	**81.434**	**81.447**	**81.776**	**81.17**	**81.586**

***Reference: 13**

Conclusion

The results show the excellent model of QSPR model was by Eq 5. with R^2= 0.998, F= 140.096 and S=0.8185by using four descriptors[nC, nO, VOLUME and S.A]was found and indicate that these descriptors have an important role in determining the properties of glass Transition Temperatures (Tg^oc)), suggest that the predicted values of glass transition temperatures (Tg^oc) influence with the values of these descriptors and showed insignificant role in QSPR model to a predict the data of the glass transition temperatures (Tg^oc). This technique shall reduce the coast, time and efforts. The satisfactory results received by QSPR modeling reveal that the QSPR a very promising machine learning technique for feature selection and mathematical modeling. This result encourages the application of QSPR to a wider selection of polymer properties and to other classes of polymers and can also be extended to other QSPR investigations.

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