Prediction of Condensation Temperatures of Substituted p-Xylylene Monomers by quantitative structure property relationships (QSPR)

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Abstract

In this work, a linear quantitative structure–property relationship (QSPR) model is presented for the prediction of condensation temperatures of Substituted p-Xylylene Monomers. The geometries of the studies compounds were optimized first at level (MM+) by molecular mechanism force field theory and then at level (AM1) by semi- empirical theory. QSPR model includes some molecular properties, regression quality indicates that these descriptors provide valuable information and have significant role in the assessment of the condensation temperatures of Substituted p-Xylylene Monomers. This model provides good results, when the model depends on four parameters [M.W, T.E, ELEC.E and I.P], with correlation coefficient $R^2 = 0.961$ for 8 p-Xylylene Monomers.

Keywords: (QSPR) model, T_{tc}, p-Xylylene Monomers

Introduction

The design of new materials with optimal thermo physical, mechanical and optical properties is a challenge for computational chemistry. Novel materials are typically developed using a trial and error approach, which is costly and time consuming [(1)]. An alternative strategy is to model the material properties as functions of the molecular structure using the so called quantitative structure–property relationships (QSPR) [(2,3)]. Application of QSPR methodologies in material design has the potential to decrease considerably the time and effort required to improve material properties in terms of their efficacy or to discover new materials with desired properties [(4)]. The QSPR approach is based on the assumption that the variation of the behavior of the compounds, as expressed by any measured physicochemical properties, can be correlated with changes in molecular features of the compounds termed descriptors [(5,6)]. The advantage of this approach lies in the fact that it requires only the knowledge of the chemical structure and is not dependent on any experimental properties. The QSPR approach has been successfully used to predict many polymeric properties, such as refractive index [(7–12)], glass transition temperature [(9,13–19)], intrinsic viscosity [(20,21)], solubility parameters [(22)] and conformational

property [23]. On the other hand the parylene N (also called poly-para-xylylene or PPX N) is the generic name for members of a unique family of thermoplastic semi-crystalline polymers that are deposited from cyclic dimer (di-p-xylylene) by the commercial Gorham method [24]. The name of parylene N, parylene C and parylene D refer specifically to the coatings produced from the Union Carbide Corporation dimers. PPX N is the reference material of the parylene families obtained from an unsubstituted cyclic ([2.2] para-cyclophane). Aromatic chlorination of the PPX N to different extents gives rise to parylene C (PPX C) and parylene D (PPX D) with one and two chlorine atoms on average per repeat unit (monomer), respectively. The chemical structure for various parylenes treated in this study is shown in Fig. 1

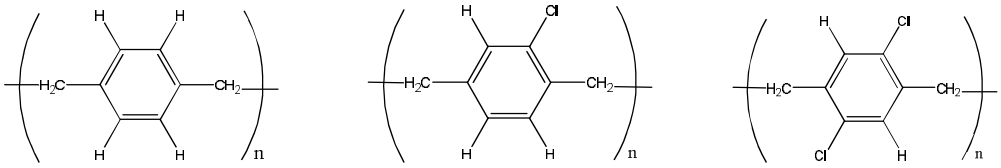

Fig. 1. Chemical structure of the most popular parylene families: parylene-N,-C and -D.

These families of parylene are particularly adapted for the electronics industry [25] and medical because of their inertness, gas phase deposition, pinholes free, conformal layers, excellent barrier properties, and room temperature deposition [26-28]. In this work we demonstrate the usefulness and focus of some of the parameters in deriving predictive QSPR models. The relation between the condensation temperatures and quantum chemical calculated parameters, Total Energy (T.E) , Heat Formation (H.F), Ionization Potential (I.P) , Molecular Weight (M.W) and Electronic Energy (ELEC.E). investigated theoretically.

Modeling and Geometry Optimization

Theoretical calculations were performed using MOPAC program version 7.00[30]. The full geometry of the compounds were optimized first at level (MM+) by molecular mechanics force field theory and then at level (AM1) by semi- empirical theory, no imaginary frequencies was found in the calculation spectra of p-Xylylene Monomers using AM1 [31]. The predictive model of QSPR study has been built up

with the help of the following descriptors in Table 2. These descriptors for the p-Xylylene Monomers under study were calculated.

Experimental

The condensation temperatures data of 8 p-Xylylene Monomers have been taken from reference [29]. The structures of p-Xylylene Monomers are shown in Table 1, and identified by the following Fig. 2. Molecular descriptors for the studied compounds: Total Energy (T.E) , Heat Formation (H.F), Ionization Potential (I.P) , Molecular Weight (M.W) and Electronic Energy (ELEC.E).

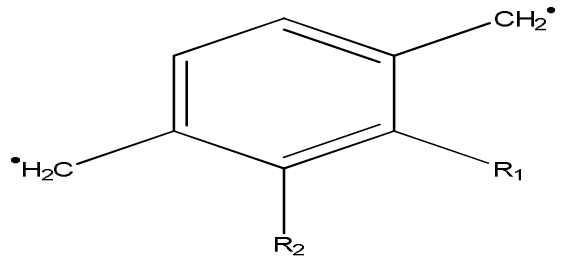

Fig. 2. Molecular structure of p-Xylylene Monomers used in the present study

Table 1: The list of chemical structure of the p-Xylylene Monomers

Compounds	R_1	R_2
I	H	H
II	CH_3	H
III	CH_2CH_3	H
IV	Cl	H
V	$COCH_3$	H
VI	CN	H
VII	Br	H
VIII	Cl	Cl

Results and Discussion

The structures of the studied compounds is shown in Figure 1, and Table 1. In this study we used parameters in Table 2. to establish the statistical correlation, the physicochemical parameters were taken as independent variables and condensation temperatures as dependent variable. The data were transferred to statistical program data fit (version9.0.59) to generate the statistically significant QSPR models. The predictive model of QSPR study has been built up with the help of the following descriptors in Table 2. These descriptors for the p-Xylylene Monomers under study were calculated.

Table 2: Calculated physico-chemical descriptors of the Monomers

Compounds	Exp	I.P ev	M.W g/mol	H.F Kcal/mol	T.E ev	ELEC.E ev
p-Xylylene	30	9.18144	106.167	4.78468	-1102.24096	-5267.13743
2-Methyl-p-ylylene	60	9.07965	120.194	-3.85622	-1251.92119	-6512.45067
2-Ethyl-p-xylylene	90	9.11336	134.221	-8.07556	-1401.40968	-7823.44662
2-Chloro-p-ylylene	90	9.19029	140.612	-1.46545	-1403.6314	-6557.04132
2-Acetyl-p-xylylene	130	9.43817	148.204	-31.9714	-1663.70549	-8926.11073
2-Cyano-p-xylylene	130	9.64311	131.177	40.66619	-1366.50648	-6896.7166
2-Bromo-p-ylylene	130	9.40415	185.063	13.00766	-1440.25118	-6554.37883
Dichloro-p-xylylene	130	9.34267	175.057	-7.23614	-1705.00105	-7936.90748

All variables are in Table 2. examinant to build the best model, the best model were selected on the basis of statistical parameters viz., Standard error of estimate (s), sequential Fischer value (F), and correlation coefficient(R), were used to evaluate the obtained QSPR. Acceptability of the regression model was judged by examining the correlation coefficient (R), Fischer value (F) and standard error of estimate (s), performing multiple liner regression analysis results in statistically significant QSPR models condensation temperatures.

The model 1(E q1) when depends on only two parameters [H.F and T.E] gave (R^2= 0.9156).

$$T_{tc} = -193.171+0.971\ H.F-0.2055\ T.E\ -0.2055$$

…….Eq1

R^2= 0.9156, s= 13.171, F = 27.148

The percentage of correlation coefficient(R^2) increases when using three parameters[T.E, I.P and H.F] as shown in eq. 2 shows very good correlation coefficient with (R^2= 0.935).

$$T_{tc} = -0.171\ T.E+47.359\ I.P+0.630\ H.F\ -584.484$$ **.....Eq2**

R^2= 0.935, s= 12.922, F = 19.200

The equation 3. when depends on three parameters [ELEC.E, I.P and M.W] shows best correlation coefficient (R^2= 0.959), while depicted in Fig. 3

T_{tc} = -1.189 E-02 ELEC.E+95.7488 I.P+0.654 M.W-968.972 …. Eq3
R^2= 0.959, s= 10.213, F = 31.540

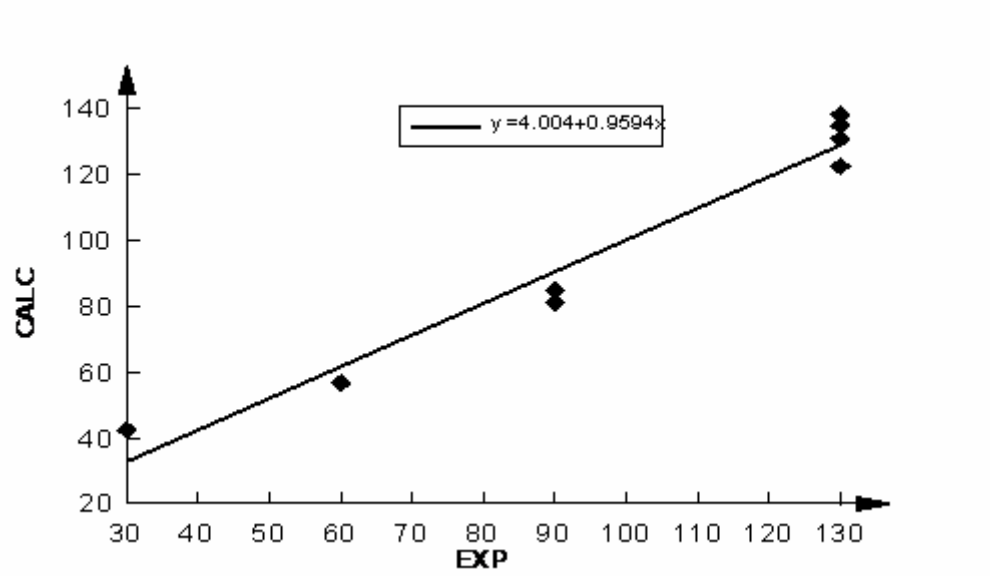

Fig. 3. Observed vs. predicted condensation temperatures of p-Xylylene Monomers calculated by Eq.3

Equation 4 . when depend on four parameters [M.W, T.E, ELEC.E and I.P] regression equation is the best produced model with very good statistical fit (R^2= 0.961) while depicted in Figures 4.

T_{tc}=0.7599 M.W+3.191 E-02T.E-1.561E-02 ELEC.E+97.4798 I.P-981.071 … Eq4

R^2= 0.961, s= 11.52, F = 18.6162

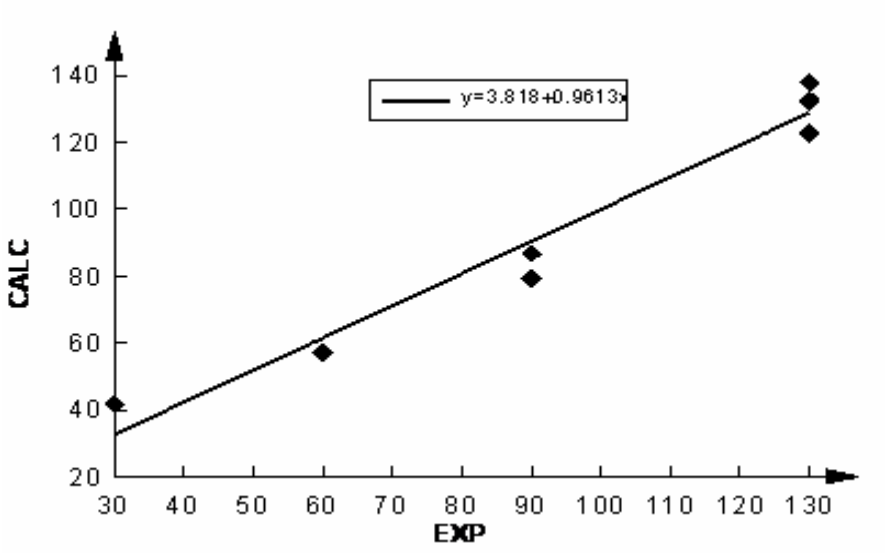

Fig. 4. Observed vs. predicted condensation temperatures of p-Xylylene Monomers calculated by Eq.4

According to the equations above, the negative signal for each T.E and ELEC.E of the shows on the existence of an inverse relationship between these variables and condensation temperatures. While the positive signal for M.W,H.F and I.P both indicate the presence of a direct correlation between these variables and condensation temperatures.

The good relationship between the experimental data and predicted condensation temperatures is reported in Table 3.

Table 3. Experimental and predicated of condensation temperatures by using Eq 1 ,Eq 2,Eq3 and Eq4 .

*Exp of condensation temperatures	Calc. by Eq1	Calc. by Eq2	Calc. by Eq3	Calc. by Eq4
30	38.02	41.91	42.316	41.66
60	60.39	57.25	56.57	57.06
90	87.02	81.75	84.57	86.7
90	93.9	89.95	81.06	79.22
130	117.7	126.93	137.95	137.84
130	127.21	131.62	122.28	122.68
130	115.49	115.47	130.61	132.63
130	150.23	145.08	134.62	132.17

*= The experimental of condensation temperatures reference(29)

The values of R2 for the QSPR models (Eqs. 1-4) range from 0.9156-0.961 which suggests that these models explain 91 -96% of the variance in the data. In addition the smaller the value of s and the larger the value of F, the better the QSPR model. The values of s in the Eq. 1-4 range from 10.213-13.171 , while the values of F range from 18.616- 31.540 statistically significant at the 96% level. The values of R2, s and F suggest that the QSPR models (Eqs. 1-4) are predictive and validate.

Conclusion

The quantum chemical calculated parameters can be successfully used for the prediction of QSPR. The study indicated that condensation temperatures of Substituted p-Xylylene Monomers can be modeled by using four parameters. The good correlation coefficients R2, depends on eq4. And the best of model which depend on the parameters M.W, T.E, ELEC.E and I.P.

References

1. K.V. Camarda and C.D. Maranas, Ind Eng Chem Res, 38, 1884 (1999).
2. A.R. Katritzky, S. Sild, V. Lobanov, M. Karelson, J Chem Inf Comput Sci, 38, 300 (1998).
3. A.R. Katritzky, S .Sild, M.Karelson. J Chem Inf Comput Sci,38,1171(1998).
4.J. Bicerano. Prediction of polymer properties. 2nd ed. New York: Marcel Dekker; 1996.
5. X.J. Yao, Y.W. Wang, X.Y. Zhang, R.S. Zhang, M.C. Liu, Z.D. Hu, B.T. Fan, Chemom.Intell. Lab. Syst. ,62 ,217(2002).
6. J. Xu, B. Guo, B. Chen, Q. Zhang, J. Mol. Model. ,12 ,65(2005).
7. J. Xu, Z. Zheng, B. Chen, Q. Zhang, QSAR Comb. Sci. ,25 ,372(2006).
8. A.R. Katritzky, S. Sild, M. Karelson, J. Chem. Inf. Comput. Sci., 38 ,1171(1998).
9. R. García-Domenech, J.V. Julián-Ortiz, J. Phys. Chem., B ,106 , 1501 (2002).
10. J. Xu, B. Chen, Q. Zhang, B. Guo, Polymer ,45 , 8651 (2004).
11. A.J. Holder, L. Ye, J.D. Eick, C.C. Chappelow, QSAR Comb. Sci. ,25,905 (2006).
12. X. Yu, B. Yi, X. Wang, J. Comput. Chem., 28, 2336 (2007).
13. C. Cao, Y. Lin, J. Chem. Inf. Comput. Sci. ,43, 643 (2003).
14. A. Afantitis, G. Melagraki, K. Makridima, A. Alexandridis, H. Sarimveis, O. Iglessi-Markopoulou, J. Mol. Struct., Theochem ,193,716 (2005).
15.X. Yu, X. Wang, H. Wang, A. Liu, C. Zhang, J. Mol. Struct., Theochem ,113,766 (2006).
16. X. Yu, B. Yi, X. Wang, Z. Xie, Chem. Phys. , 115,332 (2007).
17. C. Bertinetto, C. Duce, A. Micheli, R. Solaro, A. Starita, M.R. Tiné, Polymer ,48,7121 (2007).
18. C. Duce, A. Micheli, A. Starita, M.R. Tiné, R. Solaro, Macromol. Rapid Commun. 27,711 (2006).
19. C. Duce, A. Micheli, R. Solaro, A. Starita, M.R. Tiné, Macromol. Symp. ,13,234 (2006).
20. A. Afantitis, G. Melagraki, H. Sarimveis, P.A. Koutentis, J. Markopoulos, O. Igglessi- Markopoulou, Polymer, 47,3240 (2006).
21. F. Gharagheizi, Comput. Mater. Sci., 40, 159 (2007).
22. X. Yu, X. Wang, H. Wang, X. Li, J. Gao, QSAR Comb. Sci. ,25, 156(2006).
23. X. Yu, B. Yi, Z. Xie, X.Wang, F. Liu, Chemometr. Intell. Lab. Syst. , 87 ,247(2007).
24. W.F. Gorham, J Polym Sci A-1, 4, 3027 (1966).
25.J. Jakabovič, J.Kováč, M.Weis, D.Haško , R.Srnánek, P.Valent, et R.Resel. Microelectronics Journal,40,595(2009).
26.B. Mitu, S. Bauer-Gogoneab, H. Leonhartsbergerb, M. Lindnerb, S.Bauerb, G .Dinescua, Surf Coat Technol ,174(2003).
27. J. Miwa, Y. Suzuki, N. Kasagi, J Microelectromecanical Systems,17,611 (2008).
28.B.J. Jeon, M.H. Kim, J.C. Pyun, Sensors and Actuators B: chemical,154,89(2011).

29. F.H. Mark , Encyclopedia of Polymer Science and Technology, Vol. 10, No. 3, 2005.
30. J.FRANK SEILER RES. LAB., U.S. AIR FORCE ACADEMY, COLO. SPGS., CO. 80840.
31. Ed. K. B. Lipkowitz and D. B. Boyd, "Reviews in Computational Chemistry" , 6.Ed. K.H. Lipkowitz and D.B. Boyd, VCH(2006).

التنبؤ بدرجات حرارة التكثيف لمونمرات البارا-زايلين المعوضة بواسطة علاقات التركيب الخاصية الكمية qspr

المستخلص

في هذا العمل، تم تقديم نموذج خطي لعلاقة التركيب الخاصية الكمية (QSPR) للتنبؤ بدرجات حرارة التكثيف لمونومرات بارا- زايلين معوضة . استخدم كيمياء الكم لحساب الموصوفات لتنبأ بخواص QSPR لثمان مونمرات من بارا- زايلين معوضة. الموائمة الهندسية لهذه التراكيب أنجزت أولا بطريقة (MM+) ومن ثم أكملت الموائمة الهندسية بطريقة الشبه تجريبية (AM1). حيث تضمن موديل QSPR بعض الخواص الالكترونية والجزيئية لتنبئ بدرجات حرارة التكثيف لمونمرات البارا- زايلين. حيث أعطت المعادلة 4 التي تضمنت أربعة متغيرات[M.W,T.E, ELEC.E, I.P,]قيمة معامل ارتداد مقداره R^2 = 0.961 وهي أفضل قيمة بالمقارنة مع المعادلات السابقة وبالتالي يمكن استخدام المعادلة 4 للتنبؤ بقيم درجات التكثيف لمونمرات البارا- زايلين لمعوضات.