

A QSPR for the plasticization efficiency of polyvinylchloride plasticizers

Mridula Chandola, Sujata Marathe*

Department of Applied Science and General Engineering, Army Institute of Technology, Dighi, Pune 411015, India

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Abstract

A simple quantitative structure property relationship (QSPR) for correlating the plasticization efficiency of 25 polyvinylchloride (PVC) plasticizers was obtained using molecular modeling. The plasticizers studied were—aromatic esters (phthalate, terephthalate, benzoate, trimellitate), aliphatic esters (adipate, sebacate, azelate), citrates and a phosphate. The low temperature flex point, T_f , of plasticized polyvinylchloride resins was considered as an indicator of plasticization efficiency. Initially, we attempted to predict plasticization efficiency of PVC plasticizers from physical and structural descriptors derived from the plasticizer molecule alone. However, the correlation of these descriptors with T_f was not very good with $R = 0.78$ and $r^2 = 0.613$. This implied that the selected descriptors were unable to predict all the interactions between PVC and plasticizer. Hence, to account for these interactions, a model containing two polyvinylchloride (PVC) chain segments along with a plasticizer molecule in a simulation box was constructed, using molecular mechanics. A good QSPR equation correlating physical and structural descriptors derived from the model to T_f of the plasticized resins was obtained with $R = 0.954$ and $r^2 = 0.909$.

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1. Introduction

Glass transition temperature T_g , is one of the most important properties of amorphous polymers and perhaps the most important parameter which decides the application of non-crystalline polymers [1]. Historically, in case of polyvinylchloride (PVC) its inherent high T_g prevented it from being used in applications requiring flexibility. However, addition of plasticizer was found to lower the T_g of the polymer transforming the rigid polyvinylchloride into a flexible rubbery material, resulting in the subsequent rapid growth of the polyvinylchloride industry [2]. The principal function of the plasticizer was to reduce the modulus of the polymer at the use temperature by lowering its T_g .

The mechanism of plasticization of polyvinylchloride has been explained by various widely accepted theories like gel theory, mechanistic theory and free volume theory [3]. According to the mechanistic theory, plasticizer molecules are attracted to the polymer by forces of different magnitude so that there is a continuous exchange where by at one instant a

plasticizer molecule becomes attached to a given force center on the polymer only to be replaced by another at the next instant. This results in a dynamic equilibrium between solvation and desolvation due to which a certain fraction of force centers of the polymer chains are masked. This masking of force centers decreases the number of the loose attachments between polymer chains resulting in a subsequent increase in flexibility of chains and a corresponding lowering of T_g . According to the free volume theory, addition of a small molecule of plasticizer increases the free volume available to the polymer thus increasing the mobility of the chains. The free volume increase depends on size, shape and nature of the plasticizer molecule.

Common plasticizers used with PVC are esters of aliphatic and aromatic dicarboxylic and tricarboxylic acids and organic phosphates. For comparing the efficiency of these plasticizers the low temperature flex point T_f (where, T_f is defined as the temperature at which a composition has a modulus of 931 MPa (1.35×10^5 psi)) is frequently used [3].

A quantitative structure property relationship (QSPR) for plasticization efficiency is required to support the mechanism of plasticization and serve as a guide in design of new plasticizers or in predicting plasticization efficiency of new plasticizers.

* Corresponding author. Tel.: +91 20 27157534; fax: +91 20 27157534.
E-mail address: marathesujata@yahoo.co.in (S. Marathe).

Literature reveals a number of QSPR methods based on molecular modeling to correlate the T_g of homo- and copolymers [4–18]. There are only a few published reports [19,20] of QSPR studies wherein, T_g of more complex systems such as cross linked polymers or polymers with an additive, for example a plasticizer has been correlated. Liu et al. [19] have used group interaction modeling (GIM) for prediction of the T_g of epoxy thermosets and Tarvainen et al. [20] have used a computerized model (VolSurf) for predicting the plasticization efficiency of plasticizers used in starch acetate. There are no published reports on molecular modeling studies to obtain a QSPR for the plasticization efficiency of PVC plasticizers, hence this work was undertaken.

In this study, we have used molecular modeling to obtain a QSPR for correlating the low temperature flex point T_f of some common plasticized polyvinylchloride resins. Since this value has practical significance (ASTM D1043-72 Clash and Berg test), T_f is frequently used as an indicator of plasticization efficiency in case of plasticized polyvinylchloride resins [3].

2. Methodology

2.1. Data selection

For a good QSPR it is necessary to have a homogeneous source of data and an identical experimental protocol. We selected the data on the low temperature flex point, T_f , of plasticized polyvinylchloride resins measured under constant testing conditions as reported in Ref. [3]. T_f is defined as the temperature at which a composition has a modulus of 931 MPa (1.35×10^5 psi). A total of 52 plasticizers and their flex temperatures are listed in this reference. For our study out of the 52 plasticizers we selected those plasticizer molecules which were well defined and had a low molecular weight. Thus, data of polymeric plasticizers and mixtures of plasticizers was not used. Out of the remaining 37 structurally well-defined plasticizers modeling of some (e.g. phenylphosphates, diphenylphthalate, dicyclohexylphthalate and epoxy derivatives) was not possible due to lack of torsional data in the force field used (MM3) [21]. Hence, data of the remaining 25 plasticizers—aromatic esters (phthalate, terephthalate, benzoate, trimellitate), aliphatic esters (adipate, sebacate, azelate), citrates and a phosphate was used in this study (Table 1).

2.2. Molecular modeling

TINKER[®] [22] was used for the molecular modeling studies. Each plasticizer molecule was minimized with a RMS gradient of 0.01, using the MINIMIZE program of TINKER[®]. The force field used was MM3 [21], with the definition of “carbonyl” for carbon and oxygen of C=O bond and “ether” for the oxygen of C-O-C bond of the ester functionality. Gastegier charges were assigned to the ester functionality. The minimized plasticizer was then subjected to ANALYZE and SPACEFILL programs to obtain descriptors like total potential energy, molecular volume and effective dipole moment of the

plasticizer. These descriptors were used in the correlation and linear regression analysis studies using the Free Statistics and Forecasting Software version 1.1.20 [23].

To prepare a model of the plasticized PVC resin, first a polyvinylchloride chain segment containing ten repeat units of vinyl chloride with partly syndiotactic conformation was minimized. Gastegier charges were assigned for the chloro-functionalities. Then a simulation box of size $10 \text{ \AA} \times 10 \text{ \AA} \times 10 \text{ \AA}$ was constructed and filled with two minimized polyvinylchloride chains and one minimized plasticizer molecule and subjected to minimization again. The minimized system was then subjected to ANALYZE and SPACEFILL programs to obtain descriptors like total potential energy, molecular volume and effective dipole moment of the model. Correlation and regression analysis studies were done using the Free Statistics and Forecasting Software version 1.1.20 [23].

3. Results and discussion

In this study the low temperature flex point T_f which is frequently used as an indicator of plasticization efficiency is correlated to descriptors derived from plasticizer molecules alone as well as descriptors derived from a model.

Initially we tried to correlate T_f of plasticized PVC resins with plasticizer molecules alone. Physical descriptors, such as, mass, dielectric constant and solubility parameter and structural descriptors derived from molecular modeling of the plasticizer molecule, such as, potential energy, molecular volume, van der Waal's volume, radius of gyration, effective charge, effective dipole moment, etc., were considered. Descriptors were then preselected by removing those whose values were not available for all structures and those which gave an essentially constant value for all structures. The final QSPR model was selected on the basis of the highest correlation coefficient and lowest standard error. Four descriptors—total potential energy of the plasticizer molecule (PE) as an energy descriptor, effective dipole moment (eff.dipole) as an electronic descriptor, molecular volume (mol.vol) as a size descriptor and mass of the plasticizer were thus selected.

Using multiple linear regression analysis [23] to correlate T_f with the above four descriptors resulted in a correlation coefficient $R = 0.78$ and $r^2 = 0.613$. Table 1 shows the modeling results of the plasticizer molecules along with T_f (calculated) and T_f (observed) of the plasticized PVC resins. Fig. 1 shows the relation between the calculated and the observed T_f values and a scatter was observed as was expected from the value of r^2 . The regression equation obtained was

$$T_f = (0.7682 \pm 0.2961)PE + (72712.22 \pm 21850.09)\text{mol.vol}^{-1} + (0.0500 \pm 0.6934)\text{dipole} - (67652.57 \pm 27631.12)\text{mass}^{-1} + (188.20 \pm 27.34) \\ (F\text{-stat} = 8.24, \text{ S.E.} = 10.89, n = 23) \quad (1)$$

Table 1

Molecular modeling results for minimized plasticizer molecules and low temperature flex point, T_f of the plasticized PVC resins

Sl. no.	Plasticizer	PE (kcal/mol)	Mol.vol (Å ³)	Eff.dipole (Debyes)	Mass (amu)	T_f (experimental) (K) ^a	T_f (calculated) (K) ^b
1	Dipropylene glycol dibenzoate	22.32	309.96	0.42	342	261.0	242.22
2	Diethylene glycol dibenzoate	37.75	276.91	5.77	314	255.7	264.70
3	2,2,4-Trimethyl-1,3-pentanediol- isobutyrate benzoate	32.26	323.72	1.58	320	249.3	226.34
4	Tris(2-ethylhexyl) trimellitate	55.36	557.09	2.37	546	240.4	237.54
5	Acetyl tris- <i>n</i> -butyl citrate	18.63	462.98	11.14	486	237.0	221.01
6	Diisodecyl phthalate	41.49	419.23	9.11	418	236.0	232.21
7	Diisononyl phthalate	42.77	465.98	10.91	446	236.0	226.04
8	Ditridecyl phthalate	46.46	563.56	15.57	530	235.6	226.13
9	Tri- <i>n</i> -butyl citrate	14.02	349.83	4.62	360	234.2	219.22
10	Bis(2-ethylhexyl) phthalate	45.89	401.19	4.78	390	234.0	231.55
11	Heptyl nonyl trimellitate	49.70	539.70	10.14	560	234.0	240.89
12	Diisohexyl phthalate	33.13	330.55	5.30	334	234.0	231.43
13	Bis(2-butoxyethyl) phthalate	41.02	353.57	5.36	366	233.0	240.88
14	Butyl octyl phthalate	27.42	264.67	3.19	278	232.0	240.89
15	Dibutyl phthalate	32.35	326.30	6.28	334	232.0	233.74
16	Bis(2-ethylhexyl) terephthalate	27.82	390.69	1.83	390	231.2	222.40
17	Heptyl nonyl phthalate	35.55	387.41	8.44	390	228.1	230.24
18	Diundecyl phthalate	41.66	492.18	12.88	474	221.0	225.94
19	Butyl acetoxystearate	24.62	412.69	1.79	398	221.0	213.49
20	Diisodecyl adipate	24.45	442.75	4.59	426	210.0	212.72
21	Bis(2-ethylhexyl) adipate	29.91	383.28	0.17	370	207.0	218.14
22	Bis(2-ethylhexyl) azelate	28.50	429.26	2.94	412	205.8	215.51
23	Bis(2-ethylhexyl) sebacate	32.86	445.41	1.89	426	204.0	218.06
24	Tris(2-ethylhexyl) phosphate	13.82	459.34	6.54	434	203.0	201.65
25	Heptyl nonyl adipate	24.45	381.21	4.59	370	202.0	215.20

^a Ref. [3].^b $T_f(\text{calculated}) = 0.768 \times \text{PE} + 72712.2 \times \text{mol.vol}^{-1} + 0.05 \times \text{eff.dipole} - 67652.57 \times \text{mass}^{-1} + 188.20$.

The low value of the correlation and the regression coefficient implied that interactions between plasticizer molecule and PVC chains had to be taken into consideration in order to obtain a better correlation. Hence, to account for these interactions a model was prepared by constructing a simulation box of size 10 Å × 10 Å × 10 Å which was filled with two minimized polyvinylchloride chains of 10 monomer units each and one minimized plasticizer molecule. This model was then subjected to minimization. To allow reasonable computation time we

considered a limited polymer segment of 10 repeat units. Using multiple linear regression analysis [23] we found a good correlation between the T_f of the plasticized PVC resins and the four descriptors namely, PE, mol.vol, eff.dipole and mass. The correlation coefficient R was found to be 0.891 and regression coefficient r^2 was 0.795. Based on residuals it was observed that two plasticizers were clear outliers. These were tri-*n*-butyl citrate (bc) and acetyl tris-*n*-butyl citrate (abc). This could be because the definition used for citrate functionality in the force field used (MM3), was not appropriate. After removing the two outliers the value of correlation coefficient improved to $R = 0.954$ and regression coefficient $r^2 = 0.9106$ (F -stat = 45.84, S.E. = 5.43, $n = 23$). However, in this correlation the t -score of the mass descriptor was very low (−0.44) indicating mass was not a significant descriptor in the model. This may be because the variations in mass of model are less significant as compared to the variations in mass of plasticizers. In order to improve the model therefore, mass was deleted from the correlation. The final regression equation obtained with the remaining three descriptors was as follows

$$\begin{aligned}
 T_f &= (1.4951 \pm 0.1590)\text{PE} \\
 &+ (178727.13 \pm 33616.98)\text{mol.vol}^{-1} \\
 &+ (0.6623 \pm 0.1486)\text{eff.dipole} - (81.09 \pm 35.36) \\
 (R &= 0.9537, r^2 = 0.9096, F\text{-test} = 63.76, \\
 \text{S.E.} &= 5.36, n = 23)
 \end{aligned}
 \tag{2}$$

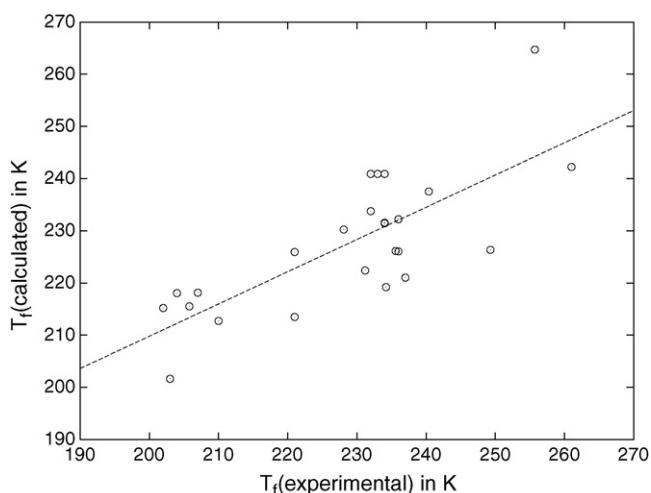
Fig. 1. Plot of T_f (experimental) vs. T_f (calculated from plasticizer molecule alone).

Table 2

Molecular modeling results for the model and low temperature flex point, T_f of the plasticized PVC resins^a

Sl. no.	Plasticizer	PE (kcal/mol)	Mol.vol (Å ³)	Eff.dipole (Debyes)	Mass (amu)	T_f (experimental) (K) ^b	T_f (calculated) (K) ^c
1	Dipropylene glycol dibenzoate	114.97	1262.76	42.10	1592	261	260.22
2	Diethylene glycol dibenzoate	112.05	1233.25	34.94	1564	255.7	254.51
3	2,2,4-Trimethyl-1,3-pentanediol-isobutyrate benzoate	116.88	1262.55	22.11	1570	249.3	249.86
4	Tris(2-ethylhexyl) trimellitate	129.78	1485.19	21.98	1796	240.4	247.84
5	Acetyl tris- <i>n</i> -butyl citrate	94.63	1407.36	15.38	1736	237	197.57
6	Diisodecyl phthalate	113.71	1364.96	12.09	1668	236	227.87
7	Diisononyl phthalate	117.02	1394.93	10.58	1696	236	229.00
8	Ditridecyl phthalate	120.76	1484.47	9.41	1780	235.6	226.08
9	Tri- <i>n</i> -butyl citrate	90.46	1299.18	8.16	1610	234.2	197.13
10	Bis(2-ethylhexyl) phthalate	118.57	1335.61	13.82	1640	234	239.16
11	Heptyl nonyl trimellitate	122.18	1470.45	16.29	1810	234	233.92
12	Diisohexyl phthalate	109.22	1276.23	12.28	1584	234	230.38
13	Bis(2-butoxyethyl) phthalate	115.22	1295.73	15.03	1616	233	239.07
14	Butyl octyl phthalate	108.44	1276.39	16.66	1584	232	232.09
15	Dibutyl phthalate	104.33	1217.13	13.55	1528	232	230.71
16	Bis(2-ethylhexyl) terephthalate	107.17	1337.07	22.07	1640	231.2	227.44
17	Heptyl nonyl phthalate	110.56	1335.89	11.17	1640	228.1	225.41
18	Diundecyl phthalate	108.05	1364.58	7.106	1648	221	216.13
19	Butyl acetoxysearate	117.55	1425.06	10.21	1724	221	226.84
20	Diisodecyl adipate	103.27	1393.76	7.53	1676	210	206.52
21	Bis(2-ethylhexyl) adipate	103.28	1333.72	10.15	1620	207	214.05
22	Bis(2-ethylhexyl) azelate	106.69	1378.35	6.00	1662	205.8	212.06
23	Bis(2-ethylhexyl) sebacate	104.82	1393.06	5.65	1676	204	207.67
24	Tris(2-ethylhexyl) phosphate	93.97	1391.33	23.66	1684	203	203.53
25	Heptyl nonyl adipate	98.60	1334.48	7.78	1620	202	205.41

^a Values obtained are for a minimized simulation box containing two polyvinylchloride chains of 10 monomer units and one molecule of plasticizer.^b Ref. [3].^c $T_f(\text{calculated}) = 1.4951 \times \text{PE} + 178727.13 \text{ mol.vol}^{-1} + 0.6623 \times \text{eff.dipole} - 81.09$.

Table 2 reports the modeling results and the calculated and observed T_f values for the plasticized polyvinylchloride resins. The t -scores of the descriptors involved in the regression equation (2) are shown in Table 3. Fig. 2 shows the plot of observed T_f and calculated T_f .

From Eq. (2) and t -scores it is seen that total potential energy of the model is the most significant descriptor with a decrease in potential energy resulting in a decrease in T_f of the resin. This is expected since a decrease in potential energy of the system implies a good interaction (solvation) of PVC chains with plasticizer molecule resulting in masking of the force centers on the PVC chains and a decrease in the loose attachments between them as proposed by the mechanistic theory.

The next significant descriptor in the model is molecular volume which showed an inverse relationship with T_f . This means an increase in mol.vol which comprises of the van der Waal's volume as well as the interstitial volume results in a corresponding decrease in T_f . This observed inverse relation supports the free volume theory of plasticization according to which an increase in free volume due to introduction of

plasticizer results in an increased mobility of polymer chains and a corresponding decrease in T_f .

The third descriptor in the correlation is effective dipole moment with an increase in dipole moment causing an increase in T_f . The larger value of dipole moment indicates stronger electrostatic attraction between chains.

The above studies indicate that the model developed correlates better with T_f as compared to the similar study with plasticizer molecules alone. Interestingly, it was observed that

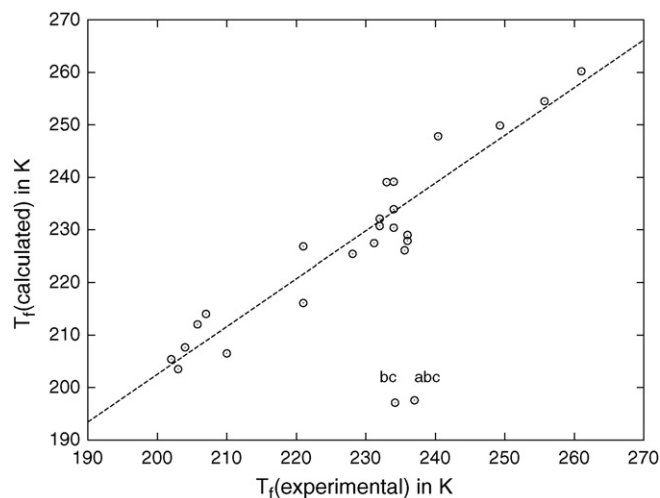
Fig. 2. Plot of T_f (experimental) vs. T_f (calculated from model).

Table 3

The t -scores of descriptors—PE, eff.dipole and mol.vol⁻¹ in Eq. (2)

Descriptor	PE	Mol.vol ⁻¹	Eff.dipole	Intercept
t -Test (Eq. (2))	9.40	5.31	4.45	-2.29
Two-tail p -value	0	3.9×10^{-5}	0.00027	0.033

the plasticizer molecule correlates well with the model. The correlation coefficient R for T_f calculated from plasticizer molecule and T_f calculated from model is 0.82. On further comparison between the individual descriptors of plasticizer molecule with corresponding descriptors derived from the model, it was found that the physical and structural descriptors correlated well (linear correlation between PE(plasticizer) and PE(model) gave $R = 0.9044$; mol.vol⁻¹(plasticizer) and mol.vol⁻¹(model) gave $R = 0.9862$) implying that the behavior of the plasticizer in the plasticized resin can be predicted from physical and structural descriptors of the plasticizer molecule alone. However, effective dipole did not correlate (linear correlation between eff.dipole(plasticizer) and eff.dipole(model) gave $R = 0.221$). This could be because effective dipole of the model arises as a result of various electronic interactions between PVC chains and plasticizer molecule and this value is independent of the value of effective dipole of the plasticizer molecule alone. Thus, effective dipole is found to be a suitable descriptor when used in the model, but more fundamental electronic descriptors need to be derived for the plasticizer molecules in order to get a good QSPR equation for plasticization efficiency directly from the plasticizers.

4. Conclusion

This paper provides an insight into the QSPR for the plasticization efficiency of PVC plasticizers using molecular mechanics. A range of PVC plasticizers namely—aromatic esters (phthalate, terephthalate, benzoate, trimellitate), aliphatic esters (adipate, sebacate, azelate), citrates and a phosphate have been correlated in this study.

We have presented a three parameter correlation for low temperature flex point, T_f , of 25 plasticized polyvinylchloride resins. We found that descriptors derived from the plasticizer molecule alone did not correlate very well with T_f ($R = 0.72$; $r^2 = 0.613$), however a good correlation ($R = 0.9537$; $r^2 = 0.9096$) was obtained using descriptors derived from the model. Plasticization of polyvinylchloride is believed to be due to solvation of the polymer chains by plasticizer molecules as well as an increase in the free volume caused by the introduction of plasticizer molecules. The main descriptors involved in the correlation, namely, potential energy (PE) and molecular volume correlate rationally to these phenomenon. A decrease in PE of the model indicates a good interaction (solvation) between the PVC chains and plasticizer molecule leading to a resultant decrease in T_f and an increase in molecular volume is interpreted as an increase in free volume leading to decrease in T_f .

Interestingly, physical and structural descriptors of plasticizer molecule alone were found to correlate well with corresponding descriptors of the model indicating that the

behavior of the plasticizer in the plasticized resin can be predicted from physical and structural descriptors of the plasticizer molecule. However, further studies are needed to obtain an improved correlation for plasticization efficiency directly from plasticizer molecule.

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References

- [1] J.E. Mark, A. Eisenberg, W.W. Graessley, L. Mandelkern, J.L. Koenig, Physical Properties of Polymers, American Chemical Society, Washington, DC, 1984 (Chapter 2).
- [2] R.C. Stephenson, Polyvinylchloride, in: H.F. Mark, N.M. Bikales, C.G. Overberger, G. Menges (Eds.), Encyclopedia of Polymer Science and Engineering, suppl. vol., 1989, p. 872.
- [3] J.K. Sears, N.W. Touchette, Plasticizers, in: H.F. Mark, N.M. Bikales, C.G. Overberger, G. Menges (Eds.) Encyclopedia of Polymer Science and Engineering, suppl. vol., 1989, p. 568.
- [4] H.G. Weyland, P.J. Hoftyzer, D.W. Van Krevelan, Polymer 11 (1970) 79–87.
- [5] D.W. Van Krevelen, Properties of Polymers: Their Correlation with Chemical Structure: Their Numerical Estimation and Prediction from Additivity Group Contributions, Elsevier, Amsterdam, 1990.
- [6] J.M. Barton, W.A. Lee, Polymer 9 (1968) 602–604.
- [7] W.A. Lee, J. Polym. Sci. 8 (Part A-2) (1970) 555–570.
- [8] J. Bicerano, Computational Modeling of Polymers, Marcel Dekker, New York, 1992.
- [9] D.R. Wiff, M.S. Altieri, I.J. Goldfarb, J. Polym. Sci. Polym. Phys. 23 (1985) 1165–1176.
- [10] A.J. Hopfinger, M.G. Koehler, R.A. Pearlstein, S.K. Tripathy, J. Polym. Sci. Polym. Phys. 26 (1988) 2007–2028.
- [11] C.J. Lee, J. Macromol. Sci. Rev. Macromol. Chem. Phys. C 29 (1989) 431–560.
- [12] T.B. He, J. Appl. Polym. Sci. 30 (1985) 4319–4324.
- [13] A.R. Katritzky, S. Sild, V. Lobanov, M.J. Karelson, Chem. Inf. Comput. Sci. 38 (1998) 300–304.
- [14] A.R. Katritzky, P. Rachwal, K. Law, M. Karelson, V.S. Lobanov, J. Chem. Inf. Comput. Sci. 36 (1996) 3879–3884.
- [15] C. Cao, Y. Lin, J. Chem. Inf. Comput. Sci. 43 (2003) 643–650.
- [16] P. Camelio, V. Lazzeri, B. Waegell, Polym. Prep. 36 (1995) 661–662.
- [17] P. Camelio, C. Cypcar, V. Lazzeri, B.J. Waegell, Polym. Sci. Part A 35 (1997) 2579–2590.
- [18] C.C. Cypcar, P. Camelio, V. Lazzeri, L.J. Mathias, B. Waegell, Macromolecules 29 (1996) 8954–8959.
- [19] H. Liu, A. Uhlherr, M.K. Bannister, Polymer 45 (2004) 2051–2060.
- [20] M. Tarvainen, R. Sutinen, M. Somppi, P. Paronen, A. Poso, Pharm. Res. 18 (2001) 1760–1766.
- [21] MM3 2000 parameter set as provided by N.L. Allinger, Univ. of Georgia, August 2000 which is available with TINKER®.
- [22] <http://dasher.wustl.edu/tinker>.
- [23] P. Wessa, Free Statistics Software, Office for Research Development and Education, version 1.1.20, 2006. URL <http://www.wessa.net/>.