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Structure-Property Study of some Phosphorus-Containing Polymers by Computational Methods

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Summary

This paper presents a structure-property study for a series of polyphosphates and polyphosphonates modeled by their dimers obtained from previous studies. Dimer structures were studied by molecular mechanics and the semiempirical AM1 method. Structural parameters were derived from the structures of minimum energy thus obtained. The influence of calculated structural descriptors of polyphosphates and polyphosphonates on their glass transition temperature was accomplished by Multiple Linear Regression (MLR). Information on the nature of structural descriptors which influence the glass transition temperature was given. Increase of the width of substituent attached to the phsphorus atom increases the glass transition temperature. Higher polymer rigidity increases the glass transition temperature. The extended form of polymer favours the increase of the glass transition temperature.

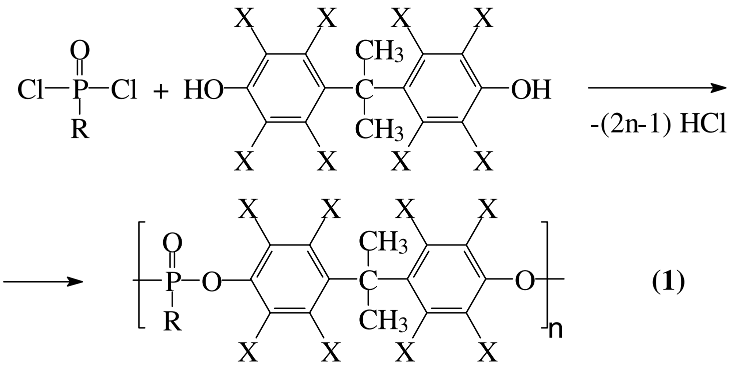
Introduction

Phosphorus-containing polymers have been found in the last years to be technically interesting as engineering plastics, especially the phosphoric polyesters (polyphosphonates and polyphosphates) because of their excellent mechanical, electrical and flame resistance properties and also because of their analogy with the nucleic acids [1, 2].

A series of polyphosphonates and polyphosphates were synthesized by base promoted liquid-vapour interfacial polycondensation of various alkyl (aryl) phosphonic (phosphoric) dichlorides with bisphenol A and tetra-halogenated bisphenol A (reaction 1). The glass-transition temperatures for the synthesized polymers were experimentally determined [3-6].

Molecular modelling [7] was used in the structure-property study of polymer flexibility, their capacity of order and also their glass transition temperatures. The semi-rigid character of polyesters has been studied by evaluating the rotational barriers measured along the internal bonds of bisphenols which compose the studied polymers.

Principal Component Analysis (PCA) was applied to study the influence of the structural monomer parameters on the glass transition temperature for a series of polymers of polyphosphate and polyphosphonate type [8].


(1)

R: CH_3, C_6H_{11}, C_6H_5, $n C_4H_9$, OC_6H_{11}, OC_6H_5, OCH_3, OnC_4H_9
X : H, Cl

Quantitative Structure-Property Relationships (QSPR) have been applied to study the influence of descriptors of low and medium molecular weight homo and copolymers on their glass transition temperatures [9]. By multiple linear regression analysis glass transition temperatures for new polymer structures was rationalized.

It is well known that for the polymers used as resins, plastics and adhesives a higher glass transition temperature is beneficial but for elastomers and polymers on liquid form a low glass transition temperature is expected.

This paper presents the influence of structural descriptors calculated for dimers of polyphosphates and polyphosphonates having the general formula I on the glass transition temperatures of the polymer using Multiple Linear Regression (MLR) [10].

Methods

Molecular structures

The polyphosphonate (phosphate) structures were modelled by their dimer obtained from previous studies [11] and are presented in Table 1.

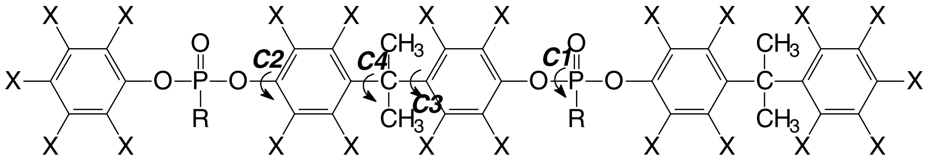
Starting structures of dimers were generated by the CHEM-X package [12] and they were energy minimized using the MM+ force field inside CHEM-X, followed by a conformational analysis using the random search procedure [13] as implemented in CHEM-X. The resulted minimized structures were completely optimized using MOPAC [14] with the semiempirical AM1 Hamiltonian [15] (eigenvector following routine (EF [16]), keyword PRECISE). For each compound the conformation of lowest energy which allowed the construction of polymer structure was considered for further calculations.

Description of dimer molecular descriptors

The experimental glass transition temperature of polymer (T_g) [3-6] was used as dependent variable for a series of 10 polyphosphates and polyphosphonates and is presented in Table 1.

Molecular descriptors derived from molecular dimer structures, like: the maximum (QMAX) and minimum (QMIN) atom charge in the dimer molecules, the HOMO and LUMO molecular orbital energies were calculated by the semiempirical AM1 method [14]. The atomic formal charge on the most positive hydrogen atom (which reflects the electrostatic part of the acidity term and expresses the hydrogen-bond acceptor basicity, Q+) and the sum of charges of the side chain atoms (R in Table 1) attached to the phosphorus atom were also employed. The difference between the maximum and minimum atomic charge in a molecule (MAXMIN) was used as a submolecular polarity parameter. Also, from the same quantum-mechanical calculations, dipole moments (μ) were considered in order to express possible dipole effects.

Table 1. The glass transition temperature (T_g) of polyphosphonates (phosphates, respectively) (I) and several structural dimer descriptors*



I

No.	R	X	T_g (°C)	G(P..P)	B_1	E_t (kcal/mol)	C1	C2
1	CH_3	H	88	9.01	1.52	13.23	81.84	-92.01
2	C_6H_{11}	H	93	9.04	1.91	12.83	78.66	-90.11
3	C_6H_5	H	99	8.97	1.71	-0.62	82.30	-93.70
4	C_6H_5	Cl	85	8.74	1.71	-3.82	77.60	-89.60
5	nC_4H_9	H	80	9.00	1.52	10.53	78.50	-91.70
6	OC_6H_{11}	H	86	8.88	1.35	17.33	88.60	-93.10
7	OC_6H_5	H	82	8.88	1.35	16.84	85.20	-93.20
8	OC_6H_5	Cl	60	8.47	1.35	15.42	70.80	-91.30
9	OCH_3	H	78	8.77	1.35	8.58	77.30	-94.20
10	OnC_4H_9	H	90	8.86	1.52	9.49	81.30	-93.00

* G(P..P)-the sum of geometrical distances between the phosphorus atoms; B_1-Sterimol parameter; E_t-torsion energy; C1- the torsion angle including the backbone phenyl ring atom bound to the oxygen atom, the two oxygen and the phosphorus atoms from the backbone; C2 - the torsion angle containing the backbone phenyl ring atom bound to the oxygen atom, the phenyl carbon atom attached to it, the oxygen and the phosphorus atoms from the backbone

Several steric, thermodynamic and hydrophobic descriptors were calculated by the ChemOffice package [17]. Among the steric parameters the Connolly Solvent Accessible Surface Area (SAS), Connolly Molecular Surface Area (MS) and Connolly Solvent-Excluded Volume (SEV) [18] were employed. The hydrophobic (ClogP) parameter and thermodynamic descriptors (like the torsion energy, E_t) and ovality were also used.

Sterimol parameters (L, B_1 and B_5) [19] and several torsion angles were used as steric descriptors. Torsion angles of atoms involved in the dimer backbone and containing the phosphorus atom (see Table 1), like: the torsion angle including the backbone phenyl ring atom bound to the oxygen atom, the two oxygen and the phosphorus atoms from the dimer backbone, C1; the torsion angle containing the backbone phenyl ring atom bound to the oxygen atom, the phenyl carbon atom attached to it, the oxygen and the phosphorus atoms from the dimer backbone, C2, were considered. The molecular weight (MW) and molar refraction (MR) calculated for the dimer and the side chain atoms attached to the phosphorus atom (R, see Table 1) were used as a measure of the bulkiness of the polyesters.

Constitutional, geometrical and functional groups descriptors were calculated by the Dragon software [20]. An indicator variable (I_{Cl}) accounting for the presence (having the value of 1) or absence (for which I_{Cl} equals zero) of chlorine atoms in the dimer was considered too.

Hydrophobic descriptor for the R substituent ($\log P_{Rekker}$) was calculated, by the Rekker fragmental method [21].

Multiple Linear Regression (MLR)

Multiple Linear Regression relates one experimental variable y_k with one or several structural variables x_i [10] by the equation:

$$y_k = b_o + \sum_i b_i \cdot x_{ik} + e_k \qquad (\mathbf{1})$$

where b represents regression coefficients and e the deviations and residuals. The leave-one-out (similar to the leave-n-out [10, 22, 23]) and leave-half-out cross validation procedure [24] was applied in order to verify the reliability of our results. In this procedure one (respectively half) of all molecules are held out from the set, the correlation equation is computed for the rest of molecules and the result is used to calculate the estimated affinity of the left out compounds and the 'predictive r^2' ($r^2_{CV\,LOO}$ and r^2_{CVLHO}, respectively). MLR calculations were performed by the STATISTICA package [25].

Results and discussion

MLR (Multiple Linear Regression) analysis has been applied to model the polymer glass transition temperature. The correlation matrix of variables included in the final MLR models is presented in Table 2.

Starting from the entire data set of structural descriptors, intercorrelations between these descriptors have been inspected. Intercorrelated variables were not included in MLR submodels and mono and bi-parametric equations were build. All the statistical tests were performed at a significance level of 5 % or less. Outliers were tested by estimating the standard residuals, as implemented in the Statistica software [25]. In addition the MLR models were also selected by the 'predictive r^2' leave-one-out cross validation criterion.

Several mono and bi-parametric MLR equations have been obtained; they are presented in Table 3. The leave-half-out cross validation procedure was used to test the predictability of the final MLR model with best statistical results. 160 calculations were performed by randomized inclusion of compounds in the two subseries.

Table 2. Correlation matrix of variables included in final MLR models*

	T_g	E_t	MEcc	G(P..P)	C1	C2	B_1
T_g	1.00	-0.39	0.14	0.81	0.62	-0.11	0.63
E_t		1.00	0.03	-0.01	0.20	-0.19	-0.53
MEcc			1.00	-0.12	0.40	0.19	0.09
G(P..P)				1.00	0.60	-0.09	0.48
C1					1.00	-0.45	-0.10
C2						1.00	0.58
B_1							1.00

* T_g represents the glass transition temperature; E_t-torsion energy; MEcc-molecular eccentricity; G(P..P)-the geometrical distance between the phosphorus atoms; C1-the torsion angle including the backbone phenyl ring atom bound to the oxygen atom, the two oxygen and the phosphorus atoms from the backbone; C2-the torsion angle containing the backbone phenyl ring atom bound to the oxygen atom, the phenyl carbon atom attached to it, the oxygen and the phosphorus atoms from the backbone; B_1-Sterimol parameter

Table 3. MLR results of dimers of the studied phosphoric polyesters*

No.	Regressional equation	N	r	SE	F	$r^2_{CV_{LOO}}$
2	T_g = -358.91 (±113.04) + 49.99 (±12.75) G(P..P)	10	0.811	6.53	15.34	0.342
3	T_g = -473.13 (±147.77) + 51.78 (±12.57) G(P..P) + 103.42 (±88.74) MEcc	10	0.844	6.39	8.69	0.359
4	T_g = -391.83 (±110.20) + 49.71 (±12.13) G(P..P) + 20.09 (±14.79) OVAL	10	0.854	6.21	9.39	0.329
5	T_g = -458.48 (±160.14) - 4.95 (± 1.61) C2 + 56.69 (±12.63) B_1	10	0.863	6.01	10.25	0.417
6	T_g = -94.51 (±26.76) + 1.49 (± 0.29) C1 + 38.23 (±7.24) B_1	10	0.936	4.20	24.76	0.665

* r - correlation coefficient, SE - standard error of estimates, F- Fischer test, and cross validated correlation coefficients $r^2_{CV_{LOO}}$ resulting from leave-one-out cross validation procedure [22]

Good correlations with the glass transition temperature have been noticed in equations containing structural parameters which reflect the polymer dimension, like: G(P..P) - the geometrical distance between the phosphorus atoms (see eq. (2)).

Molecular eccentricity and ovality of polymer influences slightly the glass transition temperature, as seen in eqs. (3) and (4), respectively. They were included in the MLR model together with the G(P..P) variable which increases the glass transition temperature. Molecular eccentricity can be related to the extended form of polymers.

Best statistical results were obtained by correlations of the glass transition temperature with the Sterimol B_1 parameter (the minimum distance to the axis along the bond between the first atom of the substituent, R, and the parent compound) and the torsion angles C2 and C1, respectively (see eqs. (5) and (6)). Best statistical results were obtained by equation (6). The leave-half-out cross validation procedure mentioned above was applied to equation (6). 54.5 % of the 'predictive r^2' values were over the value of 0.450 and 67.5 % outruns the value of 0.400. Despite the small number of compounds included in our series, the proposed equation (6) is significant. Increase of the substituent width increases the glass transition temperature. A greater B_1 value reduces the flexibility of the polymer backbone by steric hindrance. Higher polymer rigidity increases the glass transition temperature. The contribution of the torsion angles involved in these equations is smaller in comparison to that of the B_1 parameter. By the inspection of molecular structures obtained from extreme values of the torsion angles, a tendency to achieve a more extended polymer chain was observed for higher C1 values. One can suppose that the extended form of the polymer would favour the packing and would increase the glass transition temperature.

Unexpectedly, polymer hydrophobicity does not influence the glass transition temperature, as seen from the ClogP, respectively $\log P_{Rekker}$ mono-parametric models ($r = 0.499$, $SE = 9.67$, $F = 2.65$ and $r = 0.232$, $SE = 10.85$, $F = 0.46$, respectively). This fact would lead the conclusion that the oxygen atom contained in the phosphate group would be ‘hidden’ in the polymer structure. This atom is included in molecular fragments for which other descriptors included in MLR models with significant statistical results (like the C1 and the B1 Sterimol parameters) were calculated. Probably experimental data would give more accurate information on polymer hydrophobicity.

Despite the small number of investigated compounds models with significant physical interpretation were obtained. Information on the nature of structural descriptors which influence the glass transition temperature was given.

Conclusions

This paper presents a structure-property study for a series of polyphosphates and polyphosphonates. They were modeled by their dimers obtained from previous studies by molecular modeling calculations. Structural parameters were derived from the structures of minimum energy. The influence of dimer structural descriptors of polyphosphates and polyphosphonates on their glass transition temperature was accomplished by Multiple Linear Regression (MLR). Good correlations between the glass transition temperature and different structural parameters were obtained. Geometrical descriptors, like the geometrical distance between the phosphorus atoms, influence the glass transition temperature. Existence of an extended non-spherical form of polymer was observed by the inclusion of molecular eccentricity as independent variable in MLR equations with satisfactory statistical results. Increase of the substituent width increases the glass transition temperature by reducing the flexibility of the polymer backbone. Higher polymer rigidity increases the glass transition temperature. Despite the small number of investigated compounds significant MLR models were obtained. Information on the nature of structural descriptors which influence the glass transition temperature was given.

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