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QUANTUM-CHEMICAL INVESTIGATION OF CORRELATION BETWEEN THE POLAR FACTOR e AND THE CHARGE ON β-CARBON ATOM OF THE VINYL GROUP IN SUBSTITUTED STYRENES

Quantum-chemical calculations of the effective charges on β-carbon atom of vinyl group in substituted styrenes were carried out with the help of such semi-empirical methods as AM1, PM3, PM6, PM7 and RM1. Correlations between calculated values of the charges and the polar factor e in the Alfrey-Price scheme were determined. It was shown, that the best correlation gives the PM3 method, while parameterization of PM6 and PM7 methods is not suitable for parameter e prediction based on the values of the charge on β-carbon atom of vinyl group in substituted styrenes.

Keywords: quantum-chemical calculations, atom charge, Alfrey-Price scheme.

Introduction. The calculated values of effective charges on the atoms in any molecule are the most important information used in the field of theoretical organic chemistry for predicting chemical properties and mechanisms of chemical reactions. In this way, the correlations between the yield of synthetic products and the charges on atoms are widely used by chemists for the explanation of experimental data. However, the absolute values of the effective charges strongly depend on the chosen calculation method and can be used only in comparative analysis of several molecules.

It is well known, that the concept of the atom charge has its own conventionality. Actually, only the nuclear charge is localized on the atom. Inner shell electrons are situated close to the nucleuses, and the valent electrons are localized between the atoms. For atom charges calculation the electron population analysis proposed by Mulliken is commonly used in quantum chemistry [1]. Values of these charges calculated by above-mentioned method depend on the choice of basis, when we talk about ab initio calculations; if we deal with semi-empirical calculations – everything depends on the choice of the method. The atomic charges, calculated using different bases (ab initio) and different methods (semi-empirical), may differ in 1,5-2 times, but the sign and the relative value of the charge are usually remain the same. In ab initio calculations charges on atoms often increase in their absolute value, when the basis is extended.

The theory of radical polymerization considers the relationship between the structure of monomers and radicals and kinetic parameters. The solution of the problem is in attempt to determine the correlation of the relative monomer reactivity with its structure and properties of radicals. Nowadays, it is possible to solve this problem in experimental, as well as in quantum-chemical ways.

Alfrey-Price Q-e scheme was found to be very useful in a practice, due to its possibility to predict the relative monomer activities in copolymerization. It is known from the literature, that there is a clear physical interpretation of the polar nature of the parameter **e** in spite of the fact that it is semi-empirical. It follows from the linear correlation between the parameter **e** values and the value of π-electron charge on β-carbon atom of the monomer, calculated using of quantum-chemical methods [2].

Compounds, characterized by negative values of e, can be, as a rule, easily polymerized via cation mechanism, if the value is positive – via anion mechanism.

Estimation of the Q and e parameters can be based on the physical properties of the monomers. In such way, the linear correlations between LgQ and $\lambda_{\pi-\pi}$ (the absorption band maximum of the double bond in UV-spectrum of the monomer) were established. The **e** value correlates with the values of the chemical shifts of the monomer double bond, determined with the ^{13}C-NMR method.

For preliminary estimation of the monomer reactivity parameters, the quantum chemistry methods can be used, which provide possibility to predict the monomers behavior in copolymerization processes, as well as in ionic polymerization. For vinyl monomers, the monomer reactivity correlation with the charge on β–carbon atoms in ionic polymerization is observed. In case of cation polymerization, the monomer reactive capacity increases with the extension of the negative charge on the β-carbon atom of the monomer [3].

Objects and methods used in the investigation. *p*- and *m*-substituted styrenes, in which charge on β-carbon atom of the vinyl group does not strongly depend on the molecule conformation, were chosen for checking of the correlation presence between the **e** parameter value and the effective charge on β-carbon atom in monomer, calculated by the quantum-chemical methods. Silicon containing styrene, some o-substituted and disubstituted styrenes, vinylpyrimidines, vinylnaphthalene also were used; 28 monomers, which **e** parameters values of the Alfrey-Price scheme are known, were studied all together. The values of **e** parameters were taken from [2, 4–6].

The following methods were used for carrying out of the necessary calculations:

- the most popular semi-empirical quantum-chemical method AM1, [7] (parameterized with 200 compounds), which presents the proper calculations of hydrogen bonds;
- the one of the most precise method PM3, optimized with large amount of experimental data (657 molecules, 18 parameters for each element) [8];
- the most exact method for the optimization of molecules, that contain C, H and O atoms, with newer and better parameters – RM1 [9];
- the method, which is more productive and has more accurate balancing and parameterization (more than 9000 compounds used), then the previous ones. Also this method combines already mentioned advantages with the usage ab initio and DFT results, when there is the lack of experimental facts. The mistakes of AM1 and PM3 methods are fixed here, the calculations of hydrogen bonds are more precise – method PM6 [10];
- the next sizeable improvement of the MOPAC methodology – PM7 method (more than 9000 compounds used) [11]. The method, in which the new "Diffusive function" considerably improves the prediction of intermolecular interaction. It is quicker than the previous methods PM3 and PM6. In comparison with other procedures the obtained results are more exact.

All quantum-chemical calculations were carried out with MOPAC2012 program [12] and the graphic interface Winmostar was used [13].

Through the whole research the geometry of molecules was optimized with the usage of the algorithm of EF gradient lowering. Compound structures were computed with complete geometry optimization. The correspondence of the optimized structure with the minimum point on the potential energy surface was proved by the absence of imaginary frequencies in vibration spectrum. Further obtained effective charge values on β-carbon atom were used. Due to the fact that the maximum values of the potential do not always agree with the positive and negative centers positions in the molecule, and the distribution of the electrostatic potential can be more informative than the charges on atoms [14], the electrostatic potential values (ESP) has also been taken into account. The last ones were calculated according the Merz-Kollman method (MK) [15].

Experimental data discussion. The charge values on the β-carbon atoms of 28 monomers, calculated in semi-empirical approximations, are presented in Tab. 1. It was not possible to optimize the geometry of 4-trimethoxysilylstyrene molecule with RM1 method because of the lack of Si atom parameterization.

Table 1

Parameter e values and effective charges on β-carbon atom, calculated in semi-empirical approximations

№	Monomer	AM1	PM3	$PM3_{ESP}^{*}$	PM6	PM7	RM1	e
1	4-dimethylaminostyrene	-0.2176	-0.1695	-0.3137	-0.3583	-0.3239	-0.1879	-1.37
2	4-methoxystyrene	-0.2153	-0.1658	-0.2790	-0.3488	-0.3140	-0.1903	-1.11
3	2,5-dimethoxystyrene	-0.2130	-0.1561	-0.2769	-0.3358	-0.3038	-0.1864	-1.04
4	4-acetylaminostyrene	-0.2164	-0.1633	-0.2881	-0.3474	-0.3122	-0.1883	-0.9
5	4-methylstyrene	-0.2108	-0.1610	-0.2857	-0.3409	-0.3067	-0.1845	-0.98
6	4-trimethoxysilylstyrene	-0.1988	-0.1624	-0.2848	-0.3437	-0.3107	-	-0.88
7	styrene	-0.2088	-0.1581	-0.2579	-0.3259	-0.2979	-0.1813	-0.8
8	3-vinylphenol	-0.2026	-0.1523	-0.2529	-0.3046	-0.2886	-0.1722	-0.80
9	2-methylstyrene	-0.2105	-0.1588	-0.2575	-0.3436	-0.3082	-0.1847	-0.78
10	3-methylstyrene	-0.2094	-0.1588	-0.2861	-0.3214	-0.2978	-0.1813	-0.72
11	2-methyl-5-vinylpyridine	-0.2063	-0.1545	-0.2386	-0.3356	-0.2979	-0.1809	-0.58
12	4-iodostyrene	-0.1981	-0.1512	-	-0.3094	-0.2878	-0.1701	-0.4
13	3-chlorostyrene	-0.2017	-0.1505	-0.2291	-0.3076	-0.2823	-0.1701	-0.36
14	2-chlorostyrene	-0.2012	-0.1462	-0.2296	-0.3196	-0.2838	-0.1733	-0.36
15	4-chlorostyrene	-0.2026	-0.1524	-0.2455	-0.3169	-0.2889	-0.1723	-0.33
16	4-bromostyrene	-0.1990	-0.1489	-0.2194	-0.3123	-0.2882	-0.1717	-0.32
17	4-chlor-2-vinylnaphthalene	-0.2026	-0.1490	-0.3094	-0.3217	-0.2870	-0.1728	-0.31
18	2,4-difluorostyrene	-0.2005	-0.1458	-0.2902	-0.3312	-0.2929	-0.1773	-0.31
19	4-fluorostyrene	-0.2057	-0.1528	-0.2719	-0.3290	-0.2961	-0.1795	-0.3
20	3-trifluoromethylstyrene	-0.1971	-0.1430	-0.2599	-0.3093	-0.2858	-0.1681	-0.29
21	3-bromostyrene	-0.2022	-0.1492	-0.2022	-0.3094	-0.2842	-0.1715	-0.21
22	2,3-dichlorostyrene	-0.1960	-0.1404	-0.1746	-0.3066	-0.2733	-0.1651	0.09
23	4-cyanostyrene	-0.1927	-0.1391	-0.2409	-0.3000	-0.2755	-0.1629	0.26
24	3-nitrostyrene	-0.1917	-0.1387	-0.2661	-0.3046	-0.2810	-0.1635	0.3
25	4-vinylmethylbenzoate	-0.1918	-0.1415	-0.2619	-0.2916	-0.2831	-0.1631	0.4
26	4-vinylpyrimidine	-0.1852	-0.1293	-0.1618	-0.2814	-0.2566	-0.1549	0.45
27	2,5-difluorostyrene	-0.1931	-0.1317	-0.2585	-0.3082	-0.2792	-0.1639	0.73
28	4-nitrostyrene	-0.1806	-0.1200	-0.2388	-0.2805	-0.2694	-0.1509	0.81

* – the Merz-Kollman electrostatic potential values calculated in PM3 approximation.

It is well known, that the Q and e parameters values, obtained through different copolymerization reactions, are not the same. This happens because of mistakes made in determination of copolymerization constants, simplifications while scale definiton, neglect of the reaction conditions influence on the copolymerization constant values, and the acceptance of the equal e parameter value for the monomer and its radical [16].

That's why firstly we compared the charge calculation results with the help of modern semi-empirical methods in order to choose the most proper and optimal method for the next **e** parameter values estimation. The Fig. 1a shows the dependence of the effective charges on vinyl group's β-carbon atom, computed with AM1, on the effective charge values, calculated in PM3, PM6, PM7, RM1 approximations.

Analyzing Fig. 1a the following conclusions can be made:

1) Depending on the method the calculated effective charge values on atoms of all investigated monomers differ. Charges increase by their absolute value in the following order: PM3 < RM1 < AM1 < PM7 < PM6. The most overrated are the charge values, obtained with PM6 method.

2) The amplitude of the effective charge values obtained by methods like PM3, RM1 and AM1, is almost equal. If we choose PM6 or PM7, it is much greater. For the further comparison there is the dependence of the bring by value and amplitude effective charges on vinyl β-carbons (calculated with AM1) on the effective charge values, taken in PM3, PM6, PM7, RM1 approximations, presented in **Figure 1b**. Now it is possible to estimate the difference between the charge values, obtained by new semi-empirical methods compared with AM1 method results. It is clear, that the charge values computed with RM1 and AM1 are very close (standard deviation is amounts 0.0017). The difference in charge values comparing AM1 and PM3 is a bit more sizeable. The values according to the new PM6 and PM7 methods are entirely different in comparison with AM1.

For the final comparative evaluation of charges, obtained with semi-empirical methods, PM3 method was chosen as the comparison; the method which is different from AM1, but which gives similar results. The dependence of the effective charges on vinyl β-carbon atom (with PM3) on the effective charge values, calculated in AM1, PM6, PM7 and RM1 approximations is represented in Fig. 2a.

As shown, the calculated values of the effective charges on the atoms of all investigated monomers not strongly differ from the PM3 method values for AM1 and RM1, but differ extensively for the methods PM6 and PM7. For the data, shown in Fig. 2b, the difference between the charge values, calculated with all methods compared with PM3 can be evaluated. It is clear, that the values, obtained by applying RM1 and PM3, are close

quite enough to use these two methods for possible correlations analysis with **e** parameter values. Usage of new quantum-chemical methods like PM6 and PM7 is supposed to be inexact.

As the best expected correlation must be set while using PM3 method, it was also used to calculate Merz-Kollman electrostatic potential values – (ESP) on vinyl β-carbon atoms in the chosen 28 monomers. In the Fig. 3 we can see the dependence of the polar factor **e** on the effective charge values and Merz-Kollman electrostatic potential values, calculated in PM3 approximation.

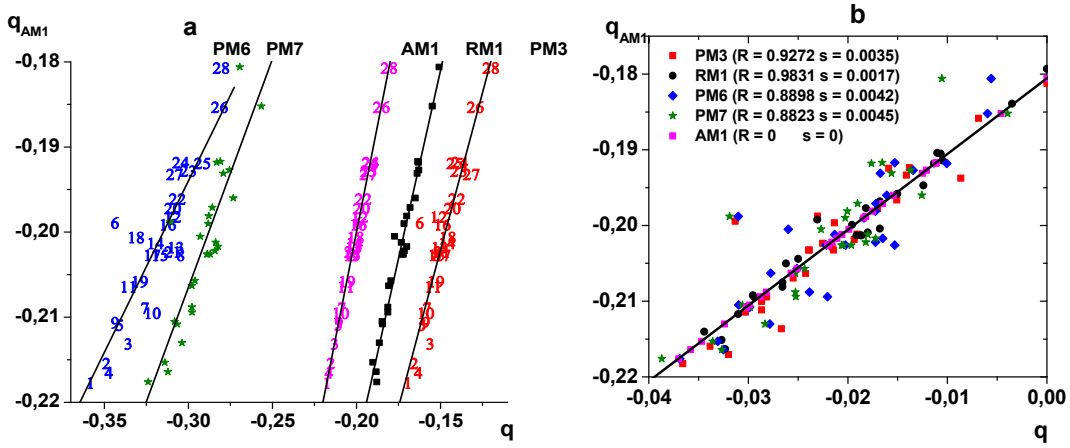

Fig. 1. Dependence of the effective charges on vinyl group β-carbon atom – a, and bring by value and amplitude effective charges on vinyl group β-carbon atom – b, calculated with AM1 method, on the effective charge values, calculated in PM3, PM6, PM7, RM1 approximations in

1 – p-dimethylaminostyrene, 2 – p-methoxystyrene, 3 – 2,5-dimethoxystyrene, 4 – p-acetylaminostyrene, 5 – p-methylstyrene, 6 – p-trimethoxysilylstyrene, 7 – styrene, 8 – m-vinylphenol, 9 – o-methylstyrene, 10 – m-methylstyrene, 11 – 2-methyl-5-vinylpyridine, 12 – p-iodostyrene, 13 – m-chlorostyrene, 14 – o- chlorostyrene, 15 – p-chlorostyrene, 16 – p-bromostyrene, 17 – 4-chlor-2-vinylnaphthalene, 18 – 2,4-difluorostyrene, 19 – p-fluorostyrene, 20 – m-trifluoromethylstyrene, 21 – m-bromostyrene, 22 – 2,3-dichlorostyrene, 23 – p-cyanostyrene, 24 – m-nitrostyrene, 25 – p-vinylmethylbenzoate, 26 – 4-vinylpyrimidine, 27 – 2,5-difluorostyrene, 28 – p-nitrostyrene

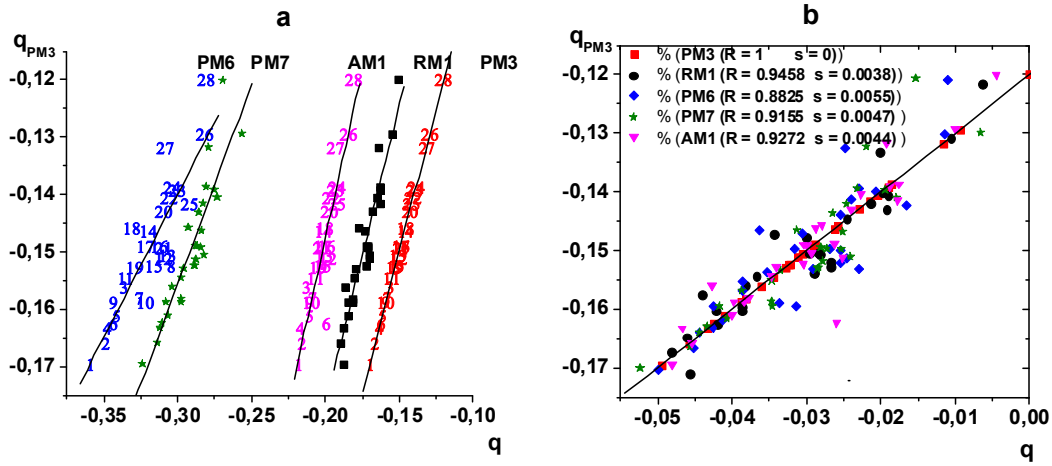

Fig. 2. Dependence of effective charges on vinyl group β-carbon atom – a, and of the reduced by value and amplitude effective charges on vinyl group β-carbon atom – b, calculated with PM3 method, on the effective charges values, computed in AM1, PM6, PM7 and RM1 approximations in

1 – p-dimethylaminostyrene, 2 – p-methoxystyrene, 3 – 2,5-dimethoxystyrene, 4 – p-acetylaminostyrene, 5 – p-methylstyrene, 6 – p-trimethoxysilylstyrene, 7 – styrene, 8 – m-vinylphenol, 9 – o-methylstyrene, 10 – m-methylstyrene, 11 – 2-methyl-5-vinylpyridine, 12 – p-iodostyrene, 13 – m-chlorostyrene, 14 – o- chlorostyrene, 15 – p-chlorostyrene, 16 – p-bromostyrene, 17 – 4-chlor-2-vinylnaphthalene, 18 – 2,4-difluorostyrene, 19 – p-fluorostyrene, 20 – m-trifluoromethylstyrene, 21 – m-bromostyrene, 22 – 2,3-dichlorostyrene, 23 – p-cyanostyrene, 24 – m-nitrostyrene, 25 – p-vinylmethylbenzoate, 26 – 4-vinylpyrimidine, 27 – 2,5-difluorostyrene, 28 – p-nitrostyrene

The scatter diagram shows that the correlation is obvious in the case of the effective charges use, and the correlation equation (1) demonstrates that the calculations allow us to value the **e** parameter for chosen monomers with the sufficient accuracy:

$$e = 6.68(\pm 0.43) + 47.04(\pm 2.88)q_{PM3}$$
$$(r = 0.9546;\ s=0.17;\ n=28) \qquad (1)$$

In this and the next ones correlation equations r – correlation coefficient, s – standard deviation, n – the number of compounds, included in correlation. As also evident from the diagram, there is no any other dependence between the electrostatic potential values and the polar factor.

Further all the chosen semi-empirical methods were compared in order to choose the optimal one for the **e** parameter values prediction. The dependence of polar factor **e** on the effective charge values, calculated in PM3, AM1, PM6, PM7 and RM1 approximations, is represented in Fig. 4.

The correlation equations, obtained from graphic data for each approximation procedure, listed below:

$$e = 11.07(\pm0.99) + 56.64(\pm4.88)q_{AM1} \quad (r = 0.9155;\ s=0.23;\ n=28) \quad (2)$$

$$e = 7.31(\pm0.90) + 24.02(\pm2.83)q_{PM6} \quad (r = 0.8577;\ s=0.30;\ n=28) \quad (3)$$

$$e = 9.31(\pm1.01) + 33.19(\pm3.46)q_{PM7} \quad (r = 0.8829;\ s=0.27;\ n=28) \quad (4)$$

$$e = 7.80(\pm0.67) + 47.26(\pm3.85)q_{RM1} \quad (r = 0.9261;\ s=0.20;\ n=27) \quad (5)$$

According to our expectations, the best correlation is observed, when we use PM3 method. AM1 and RM1 methods parameterization is almost similar, but gives slightly worse results. PM6 and PM7 methods show significant discrepancy of calculated values compared with the previous methods, as well as the poor correlation between the e parameter values of monomers and the values of their effective charges.

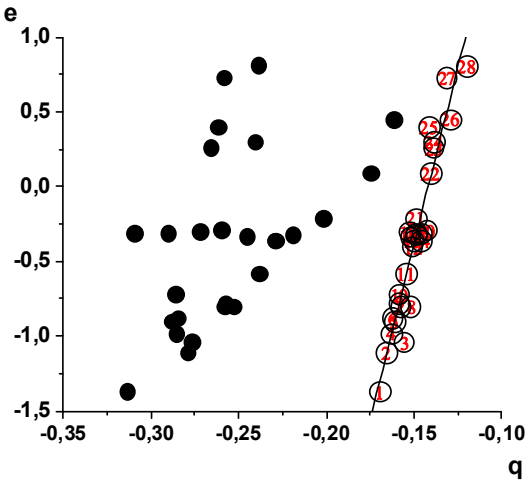

Fig. 3. Scatter diagram. Y-axis – the polar factor values. X-axis – the effective charges values on vinyl group β-carbon atom – ○ and the Merz-Kollman (MK) electrostatic potential values (ESP) – ● in
1 – p-dimethylaminostyrene, 2 – p-methoxystyrene, 3 – 2,5-dimethoxystyrene, 4 – p-acetylaminostyrene, 5 – p-methylstyrene, 6 – p-trimethoxysilylstyrene, 7 – styrene, 8 – m-vinylphenol, 9 – o-methylstyrene, 10 – m-methylstyrene, 11 – 2-methyl-5-vinylpyridine, 12 – p-iodostyrene, 13 – m-chlorostyrene, 14 – o- chlorostyrene, 15 – p-chlorostyrene, 16 – p-bromostyrene, 17 – 4-chlor-2-vinylnaphthalene, 18 – 2,4-difluorostyrene, 19 – p-fluorostyrene, 20 – m-trifluoromethylstyrene, 21 – m-bromostyrene, 22 – 2,3-dichlorostyrene, 23 – p-cyanostyrene, 24 – m-nitrostyrene, 25 – p-vinylmethylbenzoate, 26 – 4-vinylpyrimidine, 27 – 2,5-difluorostyrene, 28 – p-nitrostyrene, calculated in PM3 approximation

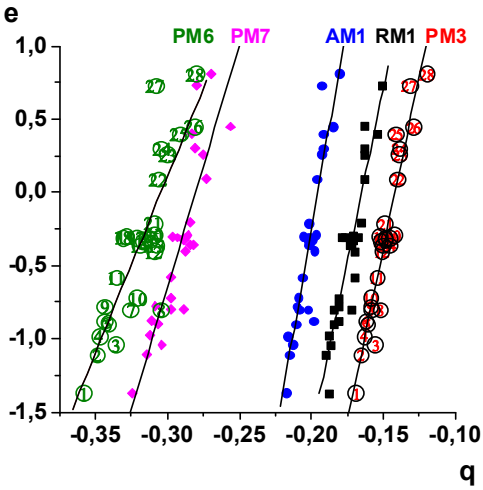

Fig. 4. Dependence of the polar factor values on the effective charges on vinyl β-carbon atom in
1 – p-dimethylaminostyrene, 2 – p-methoxystyrene, 3 – 2,5-dimethoxystyrene, 4 – p-acetylaminostyrene, 5 – p-methylstyrene, 6 – p-trimethoxysilylstyrene, 7 – styrene, 8 – m-vinylphenol, 9 – o-methylstyrene, 10 – m-methylstyrene, 11 – 2-methyl-5-vinylpyridine, 12 – p-iodostyrene, 13 – m-chlorostyrene, 14 – o- chlorostyrene, 15 – p-chlorostyrene, 16 – p-bromostyrene, 17 – 4-chlor-2-vinylnaphthalene, 18 – 2,4-difluorostyrene, 19 – p-fluorostyrene, 20 – m-trifluoromethylstyrene, 21 – m-bromostyrene, 22 – 2,3-dichlorostyrene, 23 – p-cyanostyrene, 24 – m-nitrostyrene, 25 – p-vinylmethylbenzoate, 26 – 4-vinylpyrimidine, 27 – 2,5-difluorostyrene, 28 – p-nitrostyrene, calculated in AM1, PM3, RM1, PM6 and PM7 approximations

Summary. Therefore, the electrostatic potential values, obtained by applying of semi-empirical methods, do not correlate with the polar factor values, in contrast to the effective charge values, calculated by these methods.

PM6 and PM7 semi-empirical methods parameterization is strongly different from their antecedent, PM3, and they are not suitable for atom charge calculations of organic molecules that contain C, H, O and N atoms.

The computation of charges, performed by PM3, AM1 and RM1 methods, gives on average similar charge distribution, but the best correlation value can be reached by using of PM3 method, which is recommended for approximate polar factor value prediction for substituted styrenes without conducting their copolymerization.

References

1. Mulliken R.S. J. Chem. Phys., 1955, 23(5), 1833–1842.
2. Семчиков Ю.Д. Высокомолекулярные соединения. М.: Издательский центр Академия, 2005, 368 с.
Semchikov Ju.D. High-molecular compounds. Moscow, Izdatel'skij centr Akademija, 2005, 368 p. (In Russian).
3. Рашидова С.Ш., Кудышкин В.О. Введение в химию высокомолекулярных соединений. Т.: Навруз, 2014, 194 с.
Rashidova S.Sh., Kudyshkin V.O. Introduction to the chemistry of high-molecular compounds. Tashkent, Navruz, 2014, 194 p. (In Russian).
4. Липатов Ю.С., Нестеров А.Е., Гриценко Т.М., Веселовский Р. А. Справочник по химии полимеров. К.: Наукова думка, 1971, 536 с.
Lipatov Ju.S., Nesterov A.E., Gricenko T.M., Veselovskij R. A. Handbook of Polymer Chemistry. Kiev, Naukova dumka, 1971, 536 p. (In Russian).
5. Walling C., Briggs E.R., Wolfstirn K.B., Mayo F.R. J. Am. Chem. Soc., 1948, 70, 1537-1542.
6. Lewis J. Young, J. Polym. Sci., 1961, 54, 411–455.
7. Dewar M.J.S., Zoebisch E.G., Healy E.F., Stewart J.J.P. J. Am. Chem. Soc., 1985, 107, 3902–3909.
8. Stewart J.J.P. J. Comp. Chem., 1989, 10, 209-220.
9. Rocha G.B., Freire R.O., Simas A.M., Stewart J.J.P., J. Comp. Chem., 2006, 27, 1101-1111.
10. Stewart J.J.P., J. Mol. Model., 2007, 13, 1173–1213.
11. Stewart J.J.P., J. Mol. Model., 2013, 19, 1-32.
12. Stewart J. J. P. Program Package MOPAC2009 (http://www.openmopac.net).
13. Senda N. Program Package Winmostar (http://winmostar.com).
14. Полещук О.Х., Кижнер Д.М. Химические исследования методами расчета электронной структуры молекул. Томск: Изд-во ТГПУ, 2006, 146 с.
Poleshhuk O.H., Kizhner D.M. Chemical research methods for calculating the electronic structure of molecules. Tomsk: Izd-vo TGPU, 2006, 146 p. (In Russian).
15. Singh U.C., Kollman P.A. J. Comp. Chem. 1984, 5, 129–145
16. Florjańczyk Z., Penczek S. Chemia polimerów. Tom 1. Warszawa, Politechnika Warszawska, 1995, 372 s.
Florjańczyk Z., Penczek S. Polymer Chemistry. Vol.1. Warszawa, Politechnika Warszawska, 1995, 372 p.

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КВАНТОВОХІМІЧНЕ ДОСЛІДЖЕННЯ КОРЕЛЯЦІЇ МІЖ ПОЛЯРНИМ ФАКТОРОМ e ТА ЗАРЯДОМ НА *β*-АТОМІ ВУГЛЕЦЮ ВІНІЛЬНОЇ ГРУПИ ЗАМІЩЕНИХ СТИРОЛІВ

Проведено квантово-хімічні розрахунки ефективних зарядів на β-атомі вуглецю вінільної групи в заміщених стиролах напівемпіричними методами AM1, PM3, PM6, PM7 та RM1. Встановлено кореляційні залежності між значеннями розрахованих зарядів і значеннями полярного фактора e схеми Алфрея-Прайса. Показано, що кореляція найкраща, при застосуванні методу PM3, а параметризація методів PM6 і PM7 не підходить для прогнозування параметра e за значеннями заряду на β-атомі вуглецю вінільної групи заміщених стиролів.

Ключові слова: квантово-хімічне дослідження, заряд атома, схема Алфрея-Прайса.

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КВАНТОВОХИМИЧЕСКОЕ ИССЛЕДОВАНИЕ КОРРЕЛЯЦИИ МЕЖДУ ПОЛЯРНЫМ ФАКТОРОМ e И ЗАРЯДОМ НА *β*-АТОМЕ УГЛЕРОДА ВИНИЛЬНОЙ ГРУППЫ ЗАМЕЩЕННЫХ СТИРОЛОВ

Проведены квантово-химические расчеты эффективных зарядов на β-атоме углерода винильной группы в замещенных стиролах полуэмпирическими методами AM1, PM3, PM6, PM7 и RM1. Установлены корреляционные зависимости между значениями рассчитанных зарядов и значениями полярного фактора e схемы Алфрея-Прайса. Показано, что корреляция наилучшая, при применении метода PM3, а параметризация методов PM6 и PM7 не подходит для прогнозирования параметра e по значениям заряда на β-атоме углерода винильной группы замещенных стиролов.

Ключевые слова: квантово-химическое исследование, заряд атома, схема Алфрея-Прайса.

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ХІМІЧНІ ЗАСОБИ ВПЛИВУ НА ВЛАСТИВОСТІ ФОТОАКТИВНИХ СЕРЕДОВИЩ НА ОСНОВІ ПОЛІКОМПЛЕКСІВ АЗОБЕНЗОЛУ

Розглянуто можливості зміни фізичних властивостей полімерних композитів на основі азобензолу засобами хімічної модифікації структури полікомплексів і їх складу. Основну увагу приділено вивченню можливостей впливу на характеристики електрооптичного ефекту, що спостерігається в цих композитах. Серед таких хімічних методів розглядаються, зокрема, введення в склад полікомплексу іонів металу, які є хімічно зв'язаними з полімерним ланцюгом, зміна дипольного моменту азобензольного фрагмента донорними і акцепторними домішками, введення органічного барвника до складу азобензольного полімерного композиту. Продемонстрована гнучкість властивостей досліджуваного матеріалу, яка є важливою для його практичного застосування як інформаційного або оптично активного середовища.

Ключові слова: азобензол, полімерний композит, електрооптичний ефект, поляризоване світло.

Вступ. Полімерні композити (ПК) з азобарвниками або азобензольними бічними групами розглядаються як перспективні середовища для оптичного запису і обробки інформації, а також для оптоелектронних пристроїв завдяки можливості формування в них фотоіндукованої поляризації (ФП) під впливом світла [1, 2]. При кімнатній температурі ФП може зберігатися на протязі достатньо тривалого часу. Параметри ФП можуть бути змінені під термічним або механічним впливом та у зовнішніх електричному і/або магнітному полях, а також шляхом введення спеціальних домішок до складу композитів чи іншої хімічної модифікації їх структури. Це дозволяє контролювати властивості інформаційного середовища або середовища для оптоелектроніки шляхом застосування різних зовнішніх впливів і розробляти середовища з бажаними характеристиками.

Механізм формування ФП пов'язаний із змінами ізомерних структур при поглинанні світла азобензольними групами. Молекули азобензолу можуть існувати в двох ізомерних станах: *транс*- і *цис*-ізомерів. Перехід між цими станами відбувається при опромінюванні світлом або під термічним впливом. Оптична анізотропія з'являється при зміні концентрації *транс*- і *цис*-ізомерів азобензольних груп [3,4]. Вона проявляється, зокрема, в електрооптичному ефекті, що спостерігається експериментально [4–6]. Цей ефект полягає в зміні інтенсивності лінійно поляризованого світла, що пройшло через зразок ПК, який розташований між схрещеними поляризатором і аналізатором в залежності від напруженості прикладеного зовнішнього електричного поля. Максимальний вплив електричного поля спостерігається у видимому спектральному діапазоні.

Залежність параметрів ФП в досліджуваних композитах від стану поляризації збуджуючого світла дає можливість здійснювати поляризаційний голографічний запис, що має багато переваг у порівнянні із скалярною голографією [7]. Розробка і виготовлення поляризаційно чутливих середовищ є важливою і достатньо складною проблемою. Останнім часом полімерні середовища стають дедалі популярнішими для практичного застосування завдяки їх відносній дешевизні і гнучкості параметрів. Можливості скалярного і поляризаційного голографічного запису в азобензол-містких полімерних композитах біли продемонстровані і проаналізовані [6, 8].

Метою роботи є дослідження можливостей зміни фізичних властивостей ПК на основі азобензолу шляхом хімічної модифікації структури і складу полікомплексів. Основну увагу приділено дослідженню способів впливу на характеристики електрооптичного ефекту. Серед таких хімічних методів розглядаються, зокрема, введення в склад полікомплексу іонів металу, хімічно зв'язаних з полімерним ланцюгом, зміна дипольного моменту азобензольного фрагмента донорними і акцепторними домішками, введення органічного барвника до складу ПК.