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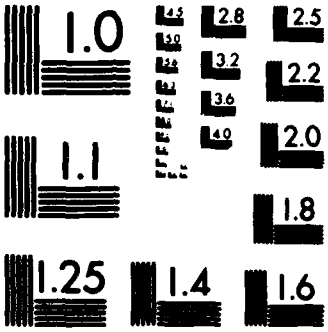
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POTENTIAL BARRIERS AND INTERNAL ROTATION IN POLYVINYL ACETATE AND POLY-o-FLUOROSTYRENE

by

Yu. Ya. Gotlib, A.A. Darinskiy

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HUMAN TRANSLATION

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В в	*В в*	V, v	Т т	*Т т*	T, t
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Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
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Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
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О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	sinh^{-1}
cos	cos	ch	cosh	arc ch	cosh^{-1}
tg	tan	th	tanh	arc th	tanh^{-1}
ctg	cot	cth	coth	arc cth	coth^{-1}
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

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POTENTIAL BARRIERS AND INTERNAL ROTATION IN POLYVINYL ACETATE AND POLY-o-FLUOROSTYRENE

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Submitted 6 June 1966

The present work is devoted to presenting the results of a calculation of potential barriers of internal rotation in the side pendant of some polymers, namely polyvinyl acetate (PVAc) and poly-o-fluorostyrene (POFS), connected namely with the steric repulsion of atoms of the side radicals and the main chain. Furthermore, for POFS it is possible to estimate the contribution to the magnitude of the potential barrier due to the interaction of atoms of neighboring chains. It is difficult to make such an estimate for PVAc, since the nearest order in this polymer is unknown. The semiempirical expressions used for the potentials of interaction of the atoms, the method and the physical and mathematical hypotheses of calculation which were used were set forth in our previous article, devoted to the

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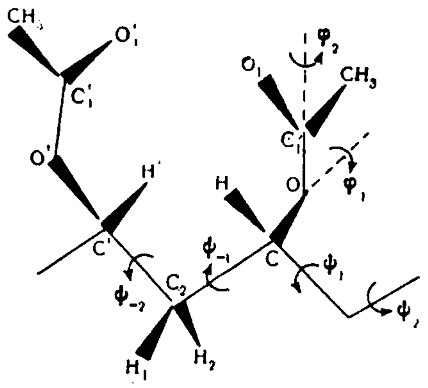
calculation of the barriers of internal rotation in the side radicals of polymethyl acrylate ~~[1]~~. (Russian Translations).



Monomer unit of PVAc in a plane syndiotactic conformation.

Polyvinyl acetate. The model of syndiotactic PVAc in a plane conformation of the chain has the following form: the structural parameters for the monomer unit of PVAc are obtained from an analysis of the conformations of low-molecular compounds which are close to vinyl acetate [2]. We accepted the following magnitudes for the values of the angles between bonds: O=C-O -125°, H-C-O -100°, C-O-C -113°, the angle between the C=C bonds is tetrahedral [3].

We are considering the rotation of a side group on the "background" of a fixed conformation of the main chain (compare [1]). Conformations of the neighboring side groups which are depicted in the diagram were selected for the calculation. As an analysis of works [3-5] shows, these are the most probable. As is evident from the drawing, the rotation in the side pendant of PVAc can take place around the C-O and O-C_1 bonds, conforming to angles of rotation φ_1 and φ_2 respectively. The calculations were made for rotation of a side group for three conformations of polymers: A - plane syndiotactic, B - convoluted syndiotactic, determined by the angles of internal rotation (-120, -120°), and C - convoluted isotactic (120.0°). All of these, as shown in work [6], are most stable in polymers of the type $(-CH_2-CHR)_n$.

Rotation around the C-O bond in conformation A is practically impossible due to the strong interaction both with the O' atom of the neighboring side pendant and with the H' atom (calculated values of the height of the barrier $U > 100$ kcal/mole). The potential curve for cases C and B is sharply asymmetric, and the height of the smaller barrier is $\sim$ 12 kcal/mole (main interaction with atoms H_1 and H_2), turning to the side of the greater barrier is impossible due to the strong interaction with the H' atom and with the continuation of the chain.

Rotation around the O-C_1 (φ_2) bond is considered in the case of two equilibrium values of φ_1 : $\varphi_1 = 0°$ and $\varphi_1 = 180°$, corresponding to the cis- and trans-position of the O-C_1 bond relative to the CH bond. When

$\varphi_1 = 0°$ the φ_2 rotation is restrained very strongly: $U > 60$ kcal/mole for B and C, $U > 150$ kcal/mole for A. Strictly speaking, with large overlapping Van-der-Waals radii of the atoms, when the energy of the interaction ~ 100 kcal/mole, the expressions for the potentials which are used by us become inapplicable. In the case of $\varphi_1 = 180°$ in conformation A the steric contribution to the barrier for rotation around O-C_1 turns out to be 6 kcal/mole, and for conformations B and C it is less than 1 kcal/mole. Naturally it has to be taken into account that the magnitudes of the barriers, especially in such conformations of the side pendant as $\varphi_1 = 180°$, will be conditioned to a considerable degree by the interchain interaction, a theoretical evaluation of which is difficult.

Dependence of U on the effective width of the potential holes.

Ψ°_{-1}	Ψ°_{-2}	$\Psi_1°$	$\Psi_2°$	$\bar{U}$, ккал/моль ①
10	10	0	0	>80
20	20	0	0	>60
10	10	10	10	>50
30	30	0	0	~50
20	20	10	10	10
30	30	10	10	7
20	20	20	20	4
30	30	20	20	2

Key: (1) kcal/mole.

As calculations show, the magnitudes of the barriers of internal rotation in the pendants of PVAc, especially in those cases when they are great, turn out to be very sensitive to small deviations of conformation of the chain from equilibrium. The table shows the dependence of the magnitude of $\bar{U}$ on the effective width of potential holes (see the previous work [1]) for φ_2 rotation when $\varphi_1 = 0^\circ$ in the plane syndiotactic conformation of PVAc. As is evident from the table, turns around the bonds of the main chain by angles $\psi_i \sim 20^\circ$ reduce the magnitude of the barrier to 10 kcal/mole, corresponding to the experimentally observed magnitudes of the barriers.

Poly-o-fluorostyrene. For evaluating the contribution of the interchain interaction to the magnitude of the barrier of internal rotation in a polymer it is necessary to have information on the method of mutual packing of chains, i.e., on the near three-dimensional order. Let us assume that the near interchain order in tightly packed sectors of an amorphous polymer corresponds to the near order in crystalline polymers, and as an example let us consider isotactic POFS - one of many polymers with flexible side groups, for which data on the three-dimensional crystalline structure are available. Unfortunately we do not have experimental data available on the dipole-radical losses for this polymer both in the amorphous and in the crystalline states, although there are data available concerning the dielectric losses in amorphous poly-2-fluoro-methylstyrene, the intrachain interaction in which is close to the intrachain interaction in POFS.

The structure of the monomer unit and the general form of crystal packing of POFS can be found in work [7]. The calculations show that both the intrachain interaction (between H and F atoms of the ring and the H atom of the neighboring monomer unit) and the interchain interaction (between the phenyl groups of neighboring chains), each individually eliminates the possibility of the transfer of phenyl rings from one equilibrium position to another for the isotactic crystalline conformation of the polymer which is being considered ($U > 100$ kcal/mole).

Internal rotation with energies of activation of $U \sim 10$ kcal/mole becomes possible when there are torsional vibrations of great amplitude present in the chain ($\sim 30^{\circ}$) and in the case of development of defects in the crystal structure, in which the minimal distance in the case of turnings between the H atoms of the phenyl groups of neighboring chains turns out to be 2.4 Å, while the normal distance between them is 1 Å. Similar defects can hardly exist at ordinary temperatures in the crystal areas of a polymer, therefore one can expect the absence of dipole-radical losses in polymers with flexible pendants in the crystalline state. At the present time only experimental data exist for crystalline polymers with rigid side groups, and it follows from these data that dipole-radical and dipole-elastic losses are connected with movement in amorphous areas. Therefore it would be interesting to set up an experiment for studying dipole-radical processes in crystalline polymers with flexible pendants.

It also follows from the results obtained that for polymers with flexible side groups of the type under consideration the dipole-radical processes may be conditioned by orientation intersectings, taking place in disintegrated sectors of the polymer, or simultaneously with disintegration. In the vitreous state these processes are probably separated: the cooperative process of disintegration of structure is manifested in the dipole-elastic relaxation process, and the dipole-radical relaxation process takes place on a background of a disintegrated state (compare [8]).

The evaluations obtained in this work and also in work [1] for the magnitudes of the barriers of internal rotation in flexible side pendants for polymethyl acrylate [1] and polyvinyl acetate may also be used with greater foundations in the consideration of the dielectric relaxation processes in solutions of polymers. The times of dielectric relaxation in solutions of polymers are determined both by the magnitude of viscous friction of the moving sectors of the chain with respect to the solvent, and by the barriers on internal rotation in the chain and in the side groups.

Conclusions

1. Calculation of the magnitudes of the potential barriers on internal rotation in the side pendant of polyvinyl acetate shows that in a plane syndiotactic conformation the magnitude of $U_{AKT} \sim 10$ kcal/mole, corresponding to experimental data, is obtained under the assumption of the presence of rotations in the main chain by angles of $\sim 20^\circ$. In other conformations of the chain the magnitude of the potential barrier, connected with internal interaction, is close to experimental. In a general case even in a separate chain the rotation

in the pendant should be correlated with other rotations.

2. The calculation made for crystalline isotactic poly-o-flurostyrene shows that for obtaining values of activation energy $U \sim 10$ kcal/mole it is necessary to assume the existence of quite large defects in the crystal structure of the polymer, i.e., dipole-radical processes in amorphous polymers may take place only with a disintegrated near order, conforming to a less dense packing than in a crystalline polymer.

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