

# INVESTIGATION OF THE STRUCTURE AND PROPERTIES OF POLY-1,3,4-OXADIAZOLES

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UDC 547.793.4

Various methods were used to investigate the peculiarities of the structure of poly-1,3,4-oxadiazoles containing diphenyleneoxide and diphenylphthalide fragments in definite molar ratios in their chains. The presence of the phthalide grouping in the poly-1,3,4-oxadiazoles has a substantial effect on the structure and properties of the polymers: intensive disintegration of the structure occurs, and the glass temperature and solubility rise. The character of the disintegration of the structure of the polymers is symbatically related to the molar fraction of phthalide fragments in the polymer chain and leads to a decrease in the deformation strength properties.

Considerable advances were recently made in the preparation of soluble heat-resistant, rigid-chain polymers – aromatic polyimides, polyarylates, polyamides, polyoxadiazoles, etc. [1-4]. In most cases, the creation of such chemical structures was associated with introduction into the polymer chain of side-chain groupings, one of the elements of which enters into the composition of the main chain of the macromolecule. In particular, effective results were achieved when polar cyclic phthalide and phthalimide groupings were introduced into the chain. Their introduction into the polymer chain is always accompanied by an increase in rigidity, which leads to an increase in the heat resistance, and by the appearance of solubility in a number of polar organic solvents [5]. Both of these facts are always bound up with the chemical nature of these groupings – their bulkiness, polarity, and specific position in the macromolecule chain.

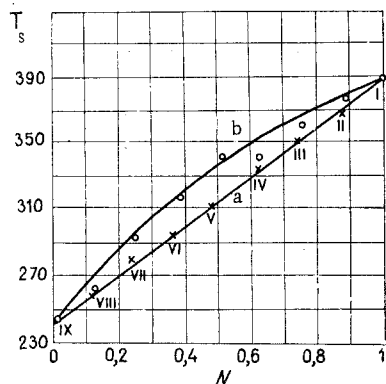


Fig. 1. Change in the softening point ( $T_s$ ) for poly-1,3,4-oxadiazoles (I-IX): a) calculated  $T_s$ ; b) experimental  $T_s$ . (N is the molar percentage of phthalide groupings in the poly-1,3,4-oxadiazoles.)

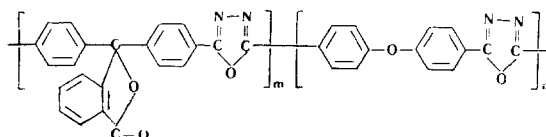
It seemed of interest to follow the character of the change in the structure and properties of polymers, especially poly-1,3,4-oxadiazoles, when a side-chain phthalide grouping is introduced and to determine their regulation. For this, we synthesized a number of poly-1,3,4-oxadiazoles in which diphenyleneoxide (DPO) and diphenylphthalidedicarboxylic acid (DPP) residues are contained in definite ratios (Table 1). The starting homopolymers in the series under consideration were, respectively, poly[2,5-(p,p'-diphenyleneoxide)]-1,3,4-oxadiazole [6], which is characterized by high flexibility of the polymer chains because of the presence in them of simple ether bonds, and poly[2,5-(p,p'-diphenylphthalide)]-1,3,4-oxadiazole [4].

A comparative investigation of the structure and properties, which was performed on a series of poly-1,3,4-oxadiazoles containing phthalide groupings in definite ratios, made it possible to follow the phenomenological picture of the changes in the structure and properties caused by the introduction of this grouping.

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TABLE 1. Ratio of Components Used for the Synthesis of Poly-1,3,4-oxadiazoles and  $\eta_r$  of the Polymers Obtained



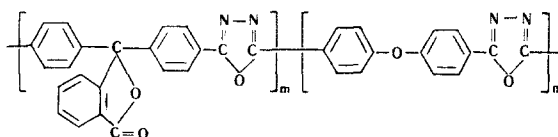
Polymer	Molar ratio of the diphenylphthalide-carboxylic acid residues in the poly-1,3,4-oxadiazoles		Starting components used for the synthesis, g					
	m	n	4,4'-diphenylphthalide-carboxylic acid	4,4'-diphenylphthalide-carboxylic acid dihydrazide	4,4'-diphenyleneoxy-carboxylic acid	4,4'-diphenyleneoxy-carboxylic acid dihydrazide	polyphosphoric acid	$\eta_r$ in a mixture of tetrachloroethylene, dl/g
I	1,000	0,000	1,870	2,010	—	—	30	1,65
II	0,875	0,125	1,870	1,507	—	0,357	29	1,78
III	0,750	0,250	1,870	1,005	—	0,715	27	1,73
IV	0,625	0,375	1,870	0,502	—	1,072	25	1,74
V	0,500	0,500	1,870	—	—	1,430	29	1,95
VI	0,375	0,625	1,402	—	0,322	1,430	28	1,94
VII	0,250	0,750	0,935	—	0,645	1,430	26	1,91
VIII	0,125	0,875	0,935	0,502	1,290	1,072	20	1,98
IX	0,000	1,000	0,935	—	1,290	1,430	20	1,68



Fig. 2. Electron microscopic photomicrographs of the surfaces of films (100–300 Å) of amorphous (a) and crystalline (b) poly[2,5-(p,p'-diphenyleneoxide)]-1,3,4-oxadiazole.

The effect on the increase in the number of phthalide groupings in the chain is manifested primarily in an increase in its rigidity, which is expressed in an increase in the softening point, determined from thermomechanical data (Table 2). This may be associated with the chemical nature of the phthalide grouping, its bulkiness and polar character, and also with its specific position in the chain. In fact, the larger phthalide group, which contains a carbon atom that is simultaneously affiliated with the major chain of the molecule, should hinder rotation of the links, and this promotes depletion of the conformational assembly of the chains. This is well illustrated in the selected system of copolymers of poly-1,3,4-oxadiazoles – poly[2,5-(p,p'-diphenyleneoxide)]-1,3,4-oxadiazole and poly[2,5-(p,p'-diphenylenephthalide)]-1,3,4-oxadiazole – since the first homopolymer contains a simple ether bond characterized by a low potential barrier to rotation and, consequently, by a comparatively high (for rigid-chain polymers) flexibility. The chain-rigidifying effect on introduction of a side-chain phthalide grouping is aggravated by the possible effect of intermolecular bonds due to orientation interaction of the dipoles caused by the carbonyl group in the phthalide ring. Thus it has been shown in the case of acrylonitrile-butadiene copolymers that the presence of sparsely situated polar groups increases the intermolecular interaction and raises the glass temperature [15]. In this case, because of the cooperative nature of the structure-forming processes that occur during glass transition, local intermolecular bonds that lead to still greater rigidification of the system [16] and,

TABLE 2. Some Physical and Physicomechanical Properties of Isotropic Poly-1,3,4-oxadiazole Films



Polymer	$\eta_r$ in a mixture of tetrachloroethylene	Breaking stress, kgf/mm <sup>2</sup>	Specific elongation on breaking, %	Softening point, T <sub>s</sub> , °C, from thermomechanical curve	Temp. of the onset of weight reduction, °C	Sorption characteristics		Solubility in organic solvents				
						free specific area with respect to p-xylylene, mg/g, S <sub>sp</sub>	total pore vol. with respect to p-xylylene, cm <sup>3</sup> /g, w <sub>0</sub>	TCE + phenol (3:1 by wt.)	trichresol	TCE <sup>a</sup>	N-MP <sup>b</sup>	DMA <sup>c</sup>
I	1,65	12,0	8	390	400—420	376	0,1862	p <sup>d</sup>	p	p	p	p
II	1,78	10,5	10	375		342	0,1778	p	p	p	p	p
III	1,73	11,3	13	365		315	0,1698	p	p	p	p	p
IV	1,74	11,7	18	335		306	0,1679	p	p	p	p	p
V	1,95	12,0	55	340		262	0,1585	p	p	p	p	p <sup>e</sup>
VI	1,94	12,0	60	315		241	0,1531	p	p	p	p	p
VII	1,91	12,8	60	290		228	0,1462	p	p	p	p	p
VIII	1,98	14,5	80	260		214	0,1422	p	p	p	p	p
IX	1,68	23,0	100	240		185	0,1216	p	p	p	p	p

<sup>a</sup>Tetrachloroethane. <sup>b</sup>N-Methylpyrrolidone. <sup>c</sup>Dimethylacetamide. <sup>d</sup>Soluble. <sup>e</sup>Insoluble.



Fig. 3. Electron microscopic photomicrograph of poly[2,5-(p,p'-diphenylenephthalide)]-1,3,4-oxadiazole after subjection to ultrasonic dispersion.

reinforcement of the intermolecular interactions. The maximum deviation is observed for poly-1,3,4-oxadiazole V. The high regularity of its structure apparently leads to an increase in the intermolecular interaction.

The presence of phthalide groupings in the polyoxadiazole chains has a substantial effect on the structure of the polymers — on their packing density. To evaluate the effect of disintegration caused by phthalide groupings in the polyoxadiazole chains, it seemed of interest to follow the change in the contraction of the calculated and experimental volumes per polymer link as a function of the chemical structure of the chain. For this, we estimated the contractions of the experimental and calculated volumes per polymer link, as well as the arbitrary contractions determined by the difference in the experimental or calculated volumes per polymer link of a poly-1,3,4-oxadiazole containing a side-chain phthalide grouping and of poly[2,5-(p,p'-diphenyleneoxide)]-1,3,4-oxadiazole.

The changes in the contractions of the volumes that we obtained (Table 3) demonstrate that the disruptions in the packing density of the polyoxadiazole chains (the disintegration effect) increase symbatically with the increase in the molar fraction of fragments that contain the phthalide grouping. In addition to the

consequently, to an increase in the softening point, can be formed. It therefore seemed of interest to compare the experimentally determined and calculated softening points (Fig. 1). The softening points (T<sub>s</sub>) for amorphous copolymers were calculated from the empirical formula [17]

$$\frac{1}{T_s} = \frac{n_1}{T_{s1}} + \frac{n_2}{T_{s2}}$$

where  $n_1$  and  $n_2$  are the weight fractions of the corresponding homopolymers, and  $T_{s1}$  and  $T_{s2}$  are the softening points of the amorphous homopolymers.

The experimental softening points, especially for poly-1,3,4-oxadiazoles V–VIII, were considerably higher than the calculated values and were not subject to the additive principle. The observed positive deviations of the experimental softening points from the calculated values are apparently associated with

TABLE 3. Change in the Contractions and Packing Density Coefficients of Poly-1,3,4-oxadiazoles I-IX

Polymer	$M_{link}$	$d_{exp}^a$ g/cm <sup>3</sup>	$V_{exp}^a$ Å <sup>3</sup>	$V_{th}^b$ Å <sup>3</sup>	$\Delta V^c$	$\Delta V_0^d$	$\Delta V_{id}$	$K, \%$ <sup>e</sup>
I	352	1,3125	446	282	164	149	86	57,9
II	338	1,3150	426	271	155	129	75	58,2
III	323	1,3150	409	260	148	112	65	58,0
IV	308	1,3030	386	249	136	89	54	64,5
V	294	1,3080	373	239	134	76	43	63,9
VI	279	1,3080	355	230	124	58	35	64,9
VII	265	1,3150	335	217	117	38	22	65,1
VIII	250	1,3150	316	206	109	19	10	65,3
IX	236	1,3155	297	196	101	—	—	66,2

<sup>a</sup>The volume per polymer link, determined from the expression  $V_{exp} = (M \cdot 10^{24} / dN) \text{Å}^3$ . <sup>b</sup>The characteristic volume per polymer link, determined as the sum of increments of the volumes of the atoms that make up the link. <sup>c</sup>Contraction volume,  $\Delta V = V_{exp} - V_{th}$ . <sup>d</sup>The arbitrary contraction determined by the difference, respectively, in the experimental and calculated volumes per polymer link of poly-1,3,4-oxadiazoles containing a side-chain phthalide grouping and of poly-[2,5(p,p'-diphenyleneoxide)]-1,3,4-oxadiazole. <sup>e</sup>Packing density coefficient in percent.

volume contractions, the packing density coefficients were calculated for the investigated series of poly-1,3,4-oxadiazoles. The character of the change in them also attests to monotonic disintegration of the polymer structure as the percentage of phthalide groupings in them increases (Table 3).

However, these regularities can be most distinctly observed when the sorption method is used to estimate the packing density. The  $S_{sp}$  and  $w_0$  values obtained on the basis of the calculation of the sorption isotherms by the Brunauer-Emmett-Teller (BET) method [18] demonstrate that the sorption capacity of these polymers is high, i.e., the surface along which sorption occurs is developed (Table 2). The development of such a porous structure may be associated with steric hindrance during packing of the polymer molecules that contain bulky phthalide groupings. The distinct correlation between the amount of side-chain phthalide groupings in the polymer chain and the specific areas and overall pore volumes may serve as a confirmation of this. The observed additivity makes it possible to assume high regularity in the arrangement of fragments along the chain and the absence of block character in the series of polymers under consideration.

The development of this sort of loosely packed structure in a solid polymer body has a substantial effect on the solubility and physicochemical properties of the poly-1,3,4-oxadiazoles (Table 2). It follows from the data presented in Table 2 that the solubility in the series of poly-1,3,4-oxadiazoles I-IX, which contain diphenylenephthalidedicarboxylic acid and diphenyleneoxidedicarboxylic acid residues in different molar ratios, decreases as the percentage of phthalide fragment decreases. As has been demonstrated, this may be associated with the increase in the porousness in the packing of the polymer chains and their aggregates due to steric hindrance caused by the presence of the phthalide ring.

The breaking elongations of the films also decrease sharply by an order of magnitude as the amount of phthalide groupings in the polymer chains increases. This sort of deterioration of the elastic properties confirms an increase in the rigidity in this series of copolymers. The tendency toward a decrease in the strength properties for approximately the same  $\eta_r$  is apparently associated with the buildup of defect character in the packing of the chains, with the porousness of the structure, and with a large quantity of micro- and macropores, which are defect portions of the material. Thus the observed tendency for the deterioration of the deformation strength properties over the investigated range of molecular weights as the percentage of phthalide groupings in poly-1,3,4-oxadiazoles increases is caused by the structure of the chain itself and by the presence of large side-chain groupings in it.

Moreover, the "magnitude of the disintegrating effect" is made up of effects associated with the "volume character" of the grouping and the increase in the rigidity of the chain as the number of phthalide groupings increases, which also leads to the formation of a looser packing. It is, however, extremely interesting that the indicated peculiarities of the microstructure do not have a substantial effect on the formation of the supramolecular structures in solid poly-1,3,4-oxadiazoles. All of the samples of copolymers of poly-

1,3,4-oxadiazoles obtained on the basis of diphenyleneoxidedicarboxylic acid, diphenylphthalidedicarboxylic acid, and poly[2,5-(p,p'-diphenylene-phthalide)]-1,3,4-oxadiazole had a fibrillar structure (Fig. 3) and remained amorphous after annealing at 300° for 10 h; i.e., they could not be thermally crystallized under these conditions. In contrast to them, poly[2,5-(p,p'-diphenyleneoxide)]-1,3,4-oxadiazole samples crystallized readily to form distinct spherulite structures (Fig. 2), observed by means of electron and light microscopy. These sorts of spherulite structures were formed on heating the films at temperatures above 240° for 5-10 min. In the process, the film became cloudy and brittle. Thus the presence of a phthalide grouping in the polyoxadiazole chains impedes only the realization of thermal crystallization and does not affect the morphology of amorphous objects.

Thus the data presented demonstrate that, in the investigated series of poly-1,3,4-oxadiazoles, a substantial contribution to the estimate of the character of the "structure-property" interrelationship is made not so much by the peculiarities of the supramolecular structure as by the specifics of the microstructure — the character of the relative spatial arrangement of the polymer chains, their packing density, etc.

## EXPERIMENTAL

The synthesis of poly[2,5-(p,p'-diphenyleneoxide)]-1,3,4-oxadiazole, poly[2,5-(p,p'-diphenylene-phthalide)]-1,3,4-oxadiazole, and of all of the copolymers was carried out by one-step polycondensation in polyphosphoric acid. The starting substances were taken in the ratios presented in Table 1, in which the reduced viscosities ( $\eta_r$ ) of 0.5% solutions of the polymers in tetrachloroethane-phenol (3:1 by weight) at 25° are also indicated.

The starting substances and polyphosphoric acid containing 84.0-84.5%  $P_2O_5$  were placed in a reactor and stirred under argon at room temperature until a finely dispersed suspension had formed (~1 h), and the mixture was then heated slowly in the course of 1.5-2 h to 140° and held at this temperature for 5 h. The resulting polymer was precipitated by pouring the reaction mixture into water. The precipitate was removed by filtration, washed with distilled water and 5% sodium bicarbonate to remove the polyphosphoric acid, and extracted with water for 24 h with subsequent washing with acetone.

The polymer was dried at 80° and reprecipitated from a 5% solution in concentrated sulfuric acid by the addition of water. It was washed with water until it was neutral and was then washed with acetone and dried in vacuo at 80°. The yield of polymer in all cases was quantitative.

All of the physicochemical tests were carried out with film samples by standard methods with a Schopper dynamometer at room temperature (Table 2). Films of the poly-1,3,4-oxadiazoles were obtained by pouring 5% solutions in tetrachloroethane or tricresol at 40-50°. The softening points were determined from thermomechanical curves recorded at a load of 0.8 kgf/cm<sup>2</sup>, and the temperature of the onset of chemical decomposition was determined from the data of dynamic thermogravimetric analysis obtained with a MOM (Hungary) derivatograph (in air at a temperature-rise rate of 3 deg/min).

The structural investigations were carried out by means of x-ray diffraction analysis, electron microscopy, and sorption and density methods.

The character of the supramolecular structure of the poly-1,3,4-oxadiazoles was investigated by means of a UÉMV-100 B electron microscope at an accelerating voltage of 75 kV. The electron microscopic investigation reduced to a study of the structure of the surface of thin (100-300 Å) polymer films [7] and to an investigation of the structure of powders and films of polymers subjected to ultrasonic dispersion with a UZDN-1 device. The dispersion products were applied to perforated collodion supports. Tinting was accomplished with Au: Pd alloy (60:40). A URS-60 device was used for x-ray diffraction analysis.

The changes in the packing density of polymers with different structures were judged from the overall pore volumes ( $w_0$ ) and the specific areas ( $S_{sp}$ ) obtained by gravimetric sorption analysis during the sorption of inert vapors (p-xylene) (Table 2). It is known that solid polymers do not undergo changes in their structure during this analysis, and the indicated characteristics consequently completely correctly reflect the polymer structure [8-10]. To determine  $S_{sp}$ , the sorption isotherms [18] were treated in accordance with the BET method for polymolecular sorption [11].

In addition, the degree of loosening was estimated from the data on the change in the contractions of the experimental and calculated molar volumes per elementary link of the polymer and from the relative packing density coefficients [12, 13]. The calculations of the contractions and packing density coefficients were performed on the basis of experimentally determined densities ( $d$ , in grams per cubic centimeter).

The characteristic volume per polymer link was estimated as the sum of the increments of the atoms that make up this link.

The experimental density was determined in a gradient density tube at  $25 \pm 0.1^\circ$  with an accuracy of up to  $0.005 \text{ g/cm}^3$  (Table 3).

Some tabulated data on the volume increments [14], as well as our calculated volume increments for nonstandard groups, were used in the determination of the calculated link volumes.

The packing density coefficients and volume contractions thus obtained are presented in Table 3.

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