

## Features of 1,4-diphenyl-butadiene distribution in *p*-terphenyl crystal lattice

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The one of the most stable and radiation-resistant organic crystals is the *p*-terphenyl one doped with diphenyl-butadiene. These crystals are used for alpha, beta and fast neutron spectrometry, selective detection of alpha and fast neutrons scintillations in the presents of gamma radiation background. At the same time the ratio of concentrations of molecules of 1,4-diphenyl-1,3-butadiene in the crystal and in the melt, their distribution along the boule are still unknown. In the present work the content of molecules of 1,4-diphenyl-1,3-butadiene in the different parts of boule was investigated. The technique of determination of 1,4-diphenyl-1,3-butadiene in a *p*-terphenyl single crystal with an accuracy to  $10^{-3}$  % has been developed.

Одними из наиболее стабильных и радиационно-стойких детекторов на основе органических монокристаллов являются монокристаллы *p*-терфенила, активированные дифенилбутадиеном. Они используются для спектрометрии  $\beta$ -излучений и быстрых нейтронов, раздельной регистрации  $\beta$ - и  $\alpha$ -излучений, нейтронов и фотонов гамма-излучения. Вместе с тем остается нерешенной проблема, связанная с определением количества дифенилбутадиена, как вводимого в расплав при выращивании, так и его распределения в буле. В работе исследовано содержание активатора в различных частях выращенной булы. Разработана методика определения дифенилбутадиена в монокристалле *p*-терфенила с точностью до  $10^{-3}$  %.

### 1. Introduction

For a long time *p*-terphenyl single crystals are known as material for detectors of ionizing radiation. It is one of the most stable and radiation-resistant organic crystals. At the same time the light yield of *p*-terphenyl is about 30 % of the light yield of anthracene, that is the reason of rare use of *p*-terphenyl crystals in scintillation engineering [1]. An introduction of 0.1 % fraction of total mass of 1,4-diphenyl-1,3-butadiene (guest molecules) in *p*-terphenyl (host molecules) melt increases the light yield of a single crystalline scintillator up to 130 % relatively to anthracene ones [2]. Studies of

radioluminescence pulse shape parameters of *p*-terphenyl single crystals with different concentration of 1,4-diphenyl-1,3-butadiene have shown that this amount of the addition agent molecules is optimal [2]. Notwithstanding this, real amount of 1,4-diphenyl-1,3-butadiene in the grown crystal was unknown.

The aim of the work is to study the variation of a probability of 1,4-diphenyl-1,3-butadiene molecules affiliation from the melt in a growing *p*-terphenyl single crystal, which can be different for various parts of boule from the cone to the top of the boule.

We have previously shown [3], that 1,4-diphenyl-1,3-butadiene molecules substitute some *p*-terphenyl molecules and the guest molecules were not distributed uniformly in the molecular crystal lattice of *p*-terphenyl growing from the melt by Bridgman-Stokbarger method. The concentration of the guest molecules increases from the cone to the top of the grown boule. The method of estimation of 1,4-diphenyl-1,3-butadiene concentration used in our previous works did not allowed precise determination of the distribution coefficient of the guest molecules.

Under the mixing of two organic molecular substances we can expect the formation of solid solutions just by substitution way. Really, molecular packing as "bump-to-hollow" with coefficient of packing equal to 0.6–0.8 shows that voids in the structure are very small in comparison with a size of molecules. Therefore filling of the voids with guest molecules, i.e. formation of interstitial solid solutions by the inclusion way is hardly possible for quite big molecules of aromatic hydrocarbons. The necessary and sufficient condition of formation of substitution solid solution crystals by two or more organic substances is shape and size proximity of molecules of initial substances [4]. Fig. 1 was drawn according to the data presented in [5] to compare the shape and size of *p*-terphenyl and 1,4-diphenyl-1,3-butadiene molecules. The figure shows that the molecules have virtually the same linear dimensions and consequently the host molecule (*p*-terphenyl) may be substituted by the guest one (1,4-diphenyl-1,3-butadiene).

## 2. Experimental

*p*-Terphenyl purified by zone melting was placed in a glass ampoule of 30 mm on inside diameter with a pre-installed seed and then 1,4-diphenyl-1,3-butadiene was added to it in terms of numbers 0.1 % of *p*-terphenyl mass fraction. The ampoule was filled with argon and placed in a vertical tube furnace with two separate heaters. Crystal growing was carried out at a rate of 1.5 mm per hour by Bridgman-Stokbarger method to complete crystallization of the melt followed by gradual cooling to room temperature. Then the ampoule was broken; the grown boule was taken out gently and was sawed into pieces in according to the schematic diagram that is demonstrated by Fig. 2. Then each of the pieces was ground. The ground samples of each of the boules

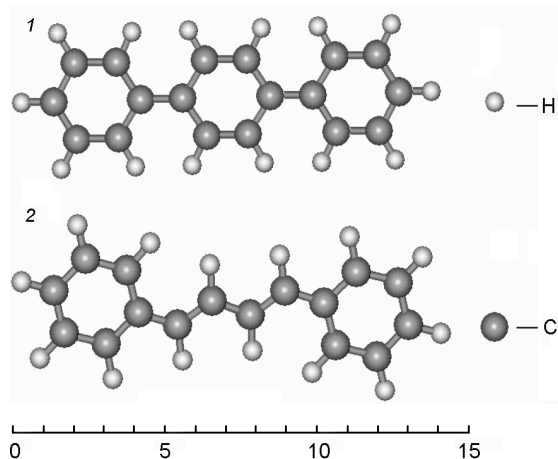


Fig. 1. The schematic representation of *p*-terphenyl and 1,4-diphenyl-1,3-butadiene molecules (distances are in Å).

pieces (Fig. 2) were analyzed by gas chromatography mass-spectrometry method.

During *p*-terphenyl single crystal growing one may expect redistribution of the guest concentration in the sample. For considered task it should be used method allowing determination of 1,4-diphenyl-1,3-butadiene concentration reliably over the range from 0.005 to 0.5 %. The gas chromatography mass-spectrometry has been chosen as such a method. The sensitivity of the method to the individual components of the mixture may be increased using determination by selected characteristic ions of the components.

*p*-Terphenyl is an organic material with relatively high melting temperature. It is also poorly soluble in most organic solvents at room temperature. Therefore an extraction of 1,4-diphenyl-1,3-butadiene was run by heating the sample in *o*-xylene until its complete dissolution followed by crystallization of excess *p*-terphenyl. The determination of 1,4-diphenyl-1,3-butadiene concentration was carried out from the mother liquor. It reduced significantly amount of the main component of the mixture (*p*-terphenyl) in the solution and thereby decreased its influence during the chromatographic analysis. Losses of the measuring component (1,4-diphenyl-1,3-butadiene), for instance, caused by co-crystallization with *p*-terphenyl was taken into account during the calibration procedure.

The calculation of 1,4-diphenyl-1,3-butadiene concentration was carried out by the method of internal standard. The internal standard has to satisfy the following requirements [6]:

– to have volatility similar to that of the substance being determined;

– to have a well-resolved peak located at the chromatogram near the peak of the substance being determined, but not overlapped it.

– to absence at the mixture under analysis;

– to dissolve well in the mixture under analysis;

– not to react with other components of the sample.

On the basis of the results of preliminary chromatographic studies we have chosen anthracene as a standard, which satisfies whole the aforementioned requirements. The amount of anthracene added to the solutions under investigation was commensurate with the expected amount of the component being analysed. Analyses were carried out by the gas chromatography mass-spectrometer Varian 1200L (an ionization by electron impact, ionization energy is 70 eV). It was used the capillary column Optima-5 (Macherey-Nagel), phase — poly (5 % diphenyl / 95 % of dimethylsiloxane). We used the following temperature program: isotherm at 100°C for one minute, heating to 300°C at a rate of 20°C per 1 min. The volume of the introduced sample was 1 micro litre; injector temperature was 300°C. Accurately weighted samples were used for preparation of working and calibration solutions and concentrations of corresponding components were calculated. Working solutions of 0.0002 g/ml anthracene and 1,4-diphenyl-1,3-butadiene were prepared by dissolving the pure substance in *o*-xylene. The working solutions were used for preparation of the calibration solutions with concentration of anthracene and 1,4-diphenyl-1,3-butadiene from 0.02 % to 0.1 %. To prepare solutions for investigation, 0.5 g of *p*-terphenyl sample being investigated was put in a test-tube, than 0.5 ml of the working solution of anthracene and 2.5 ml of *o*-xylene were added. The calibration solutions and the solutions being investigated were heated until *p*-terphenyl complete dissolution and left for twenty-four hours for crystallisation. Before the analysis the solutions were shaken, let the *p*-terphenyl sediment settle or was precipitated by a centrifuge if necessary and then the liquid above the sediment was analyzed. The result of determination of 1,4-diphenyl-1,3-butadiene concentration for each *p*-terphenyl sample is arithmetic average of the results of three analyses . It

Tables. Content of 1,4-diphenyl-1,3-butadiene in the samples

The samples	Content of 1,,4-diphenyl-1,,3-butadiene $\omega \pm \Delta\omega$ , %
4	0.15±0.06
3	0.062±0.019
2	0.036±0.004
1	0.021±0.006
(κ) cone	0.025±0.009

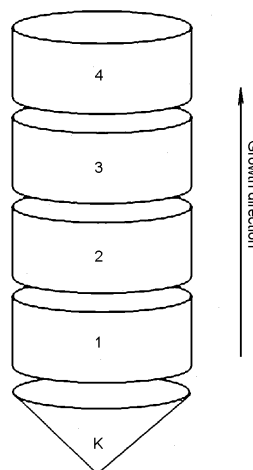


Fig. 2. The scheme of sawing of the grown bulk and numbering of the samples (it corresponds to the numbering in Table).

was obtained at least three chromatograms for each solution. The results of determination of 1,4-diphenyl-1,3-butadiene concentration in *p*-terphenyl samples are presented in Table.

### 3. Results and discussion

The results presented in Table shows that 1,4-diphenyl-1,3-butadiene concentration in the grown boule is not uniform but rises from the boule cone to it top. The minimum of 1,4-diphenyl-1,3-butadiene concentration is 0.02 % of *p*-terphenyl mass fraction that is almost one-fifth of its initially introduced concentration. Therefore part of the guest substance was driven back into the melt during the crystal growing. More active substitution of *p*-terphenyl molecules by the guest molecules occurred after increasing the 1,4-diphenyl-1,3-butadiene concentration in the growing crystal. The guest concentration exceeded that originally introduced into the melt at the top of the boule and preferential precipitation of the guest crystalline grains was observed.

### 4. Conclusions

The gas chromatography mass-spectrometry method used in the work allowed us to

determine 1,4-diphenyl-1,3-butadiene concentration in *p*-terphenyl single crystals grown from the melt. It has been shown that 1,4-diphenyl-1,3-butadiene concentration increases with height of the grown boule from the cone to the top. The determination method of 1,4-diphenyl-1,3-butadiene in a *p*-terphenyl single crystal with an accuracy to  $10^{-3}$  % has been developed. It was found that the minimal value of 1,4-diphenyl-1,3-butadiene concentration is equal  $(0.021 \pm 0.006)$  %, while the introduced concentration in the melt is 0.1 %.

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## Особливості розподілу 1,4-дифеніл-1,3-бутадієну у кристалічній ґратці *n*-терфенілу

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Одним з найбільш стабільних та радіаційно-стійких детекторів на основі органічних монокристалів є монокристали *n*-терфенілу, активовані дифенілбутадієном. Вони використовуються для спектрометрії  $\beta$ -випромінювання та швидких нейтронів, роздільної реєстрації  $\beta$ - і  $\alpha$ -випромінювання, нейтронів та фотонів гамма-випромінювання. Разом з тим залишається невирішеним питання, пов'язане з визначенням кількості дифенілбутадієну, що був введений у розтоп при вирощуванні, і його розподілу вздовж булі. У роботі досліджено вміст активатора у різних частинах вирощеної булі. Розроблено методу визначення дифенілбутадієну у монокристалі *n*-терфенілу з точністю до  $10^{-3}$  %.