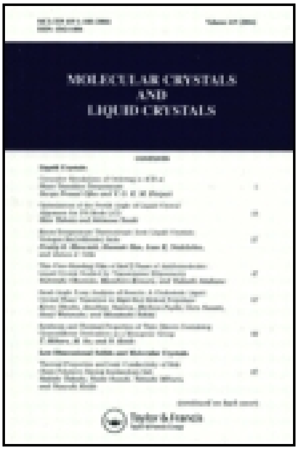


Molecular Crystals and Liquid Crystals

Pentazadienes as New Photoinitiators in the Development of New Materials

Nataliya Yeshchenko [a] & Volodymyr Syromyatnikov [a]

[a] Kyiv National Taras Shevchenko University, Macromolecular Chemistry Department, Kyiv, Ukraine

Version of record first published: 31 Aug 2006

To cite this article: Nataliya Yeshchenko & Volodymyr Syromyatnikov (2005): Pentazadienes as New Photoinitiators in the Development of New Materials, Molecular Crystals and Liquid Crystals, 427:1, 169/[481]-179/[491]

To link to this article: http://dx.doi.org/10.1080/15421400590892172

Mol. Cryst. Liq. Cryst., Vol. 427, pp. 169/[481]–179/[491], 2005

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590892172

Pentazadienes as New Photoinitiators in the Development of New Materials

Nataliya Yeshchenko
Volodymyr Syromyatnikov
Kyiv National Taras Shevchenko University, Macromolecular Chemistry Department, Kyiv, Ukraine

Investigations of volume photopolymerization in big diameter round dilatometer are carried out. The methods of experiment allowing in regular intervals to irradiate a solution from different sides are offered. The theory of photopolymerization processes for any values of initiator optical density is proposed.

On the basis of theoretical and experimental studies of a photoinitiated polymerization by pentazadienes is shown, that photopolymerizations kinetics at initiator big values of optical density contains fast and slow components, and the fast one corresponds to dilatometer surface polymerization, and the slow one – to reaction front movement inside the dilatometer. It is shown, that due to computer simulation of photopolymerization kinetics molecular weight distribution is possible to calculate. It is found, that during the polymerization distribution of macromolecules yields on polymeric chain lengths is kept constant.

Keywords: initiators; pentazadienes; photopolymerization

INTRODUCTION

Pentazadienes represent a class of new light-sensitive [1] organic compounds, which can form some kinds of free radicals with different reactivities on UV-exposure. These reactivities depend on an electronic structure of pentazadienes and radicals. Using photoinitiators of different structures and varying of photopolymerizations conditions it is possible to develop polymeric composites for electronics with optimal

---

Financial support from Ukrainian Ministry of Science and Education (grant No. F7/347–2001) is gratefully acknowledged.

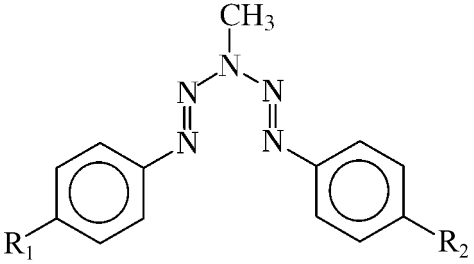
Address correspondence to V. Syromyatnikov, Kyiv National Taras Shevchenko University, Macromolecular Chemistry Department, 60 Volodymyrska Str., Kyiv 01033, Ukraine. Tel.: +38044-2393300, E-mail: svg@chem.univ.kiev.ua

properties. For manufacturing of optical devices a valume polymerization is commonly used, therefore it is very important clarify peculiarities of regulated volume photopolymerization which can be possible due to an application of pentazadienes as photoinitiators.

EXPERIMENTAL

Materials

In this work the new class of photoinitiators – 3-methylpentazadienes-1,4 of the common formula is suggested:



where **I** – $R_1 = R_2 = H$, **II** – $R_1 = R_2 = OCH_3$, **III** – $R_1 = R_2 = NO_2$. They were syntesized by an interaction of suitable diazotized aromatic amines with methylamine.

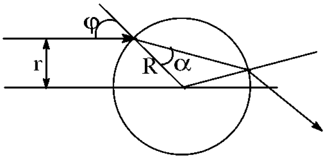
Methods

Traditionally in researches of photopolymerization kinetics for vinyl monomers quartz dilatometer of small thickness are used. For this aims a solution of monomer and initiator of polymerization are chosen in a such way that the optical density of resulting solution on wave length of irradiation is small ($D \leq 0{,}01$). Under such conditions it is possible to consider, that the light intensity for the initiator of polymerization can be the same in all points of a solution. As scientific researches are carried out with a wide set of concentrations of the initiator and a monomer, it is necessary to take many of dilatometers with various thickness, that not always possible. If we use only one dilatometer, it is necessary to pay an attention on results of processing of experimental dependence of light intensity of initiated polymerization from a route of light in a solution. Of course, it complicates our results of processing. However, the theory of such processes isn't too complicated and using of computers allows bypassing arising difficulties at results processing [1].

In contrast to dilatometer with rectangular section for which it is convenient to carry out calculations of photochemical processes, for cylindrical dilatometers which are frequently used in the practice, the theory of photopolymerization kinetics is not developed, that is why the method has no adequate mathematical processing. Therefore in this work we have decided to clarify this problem.

The irradiation of cylindrical dilatometer with a beam directed perpendicularly to an axis of the dilatometer, results that the intensity of light falling onto a solution, depends on a distance from an axis of the beam which is passing through an axis of a dilatometer:

$$I(r) = I_0 \cos(\varphi) = \frac{I_0\sqrt{R^2 - r^2}}{R},$$



where R – radius of a dilatometer, r – distance from an axis of a beam.

The beam entering the dilatometer, refracts according to optical laws: if the angle between a falling beam and radius in a point of falling of beam is equal φ, than the refracted beam will pass at the angle of α to radius, and $\sin\alpha = \sin\varphi/\mathrm{n}$, where n – a parameter of refraction of a solution in dilatometer (for example, for dimethylformamide $\mathrm{n} = 1{,}43$). Thus it appears, that the light inside dilatometer is focused, and so distorts the law of dependence of light intensity distribution from distance. Besides parts of the dilatometer, located above and below limiting beams which are entered in the dilatometer at $\varphi = 90^\circ$, is found unlit. Of course, dispersion of light always exists and the photopolymerization will proceed in all points of a solution. However it appears practically impossible to take into account all processes in round dilatometer while it irradiates from a dot light source.

So we have suggested to change the scheme of a solution irradiation so that all points of a surface of a dilatometer have to be in identical conditions. For this purpose we have considered some schemes of irradiation. Especially, usage of elliptic irradiator has allowed to show (Fig. 1a), that all the surface of a cylindrical dilatometer is illuminated. However, as follows from Figure 2, in this case the surface of a dilatometer is illuminated essentially non-uniformly, that creates the certain difficulties with an interpretation of the experiment. Especially, it will be problematic to investigate a dependence of the polymerization speed on the intensity of an illumination.

It seems, that disadvantages of the first lighting scheme by the second one substantially liquidates (Fig. 1b) in which the illuminator

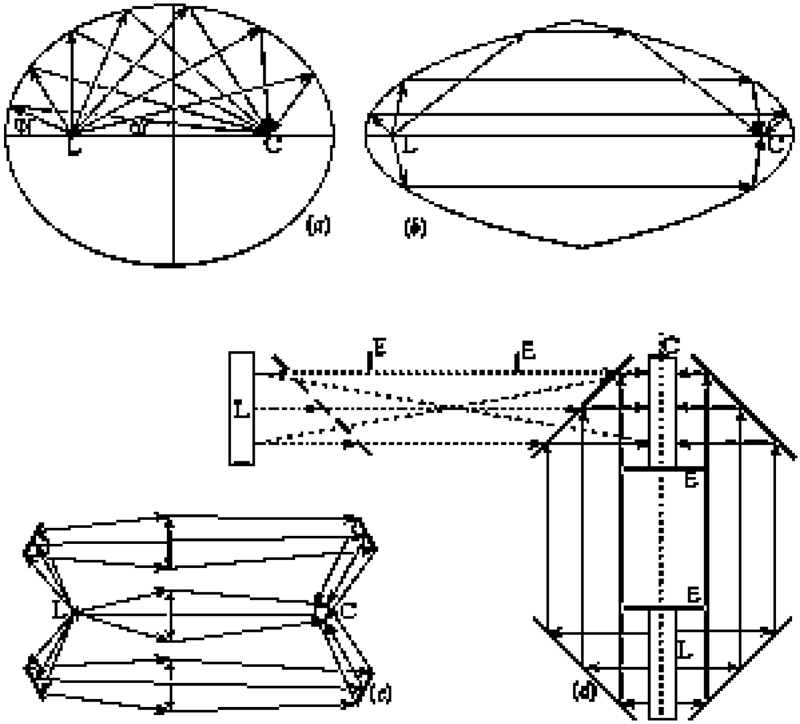
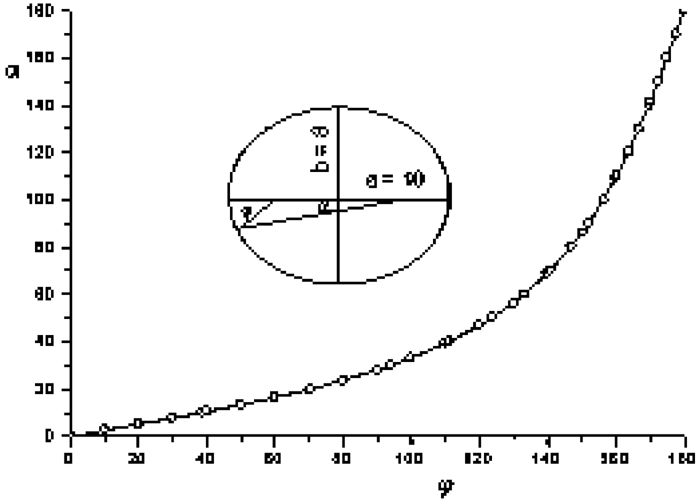


FIGURE 1 Schemes of illuminators for research of photopolymerization in a circular dilatometer.

is presented by two parabolic reflectors. However, such reflector allows uniform the distribution of light intensity for a small interval of the radiation angles corresponding to an angle of disclosing of a cylindrical paraboloid except for a part which is in a shadow of a sample.

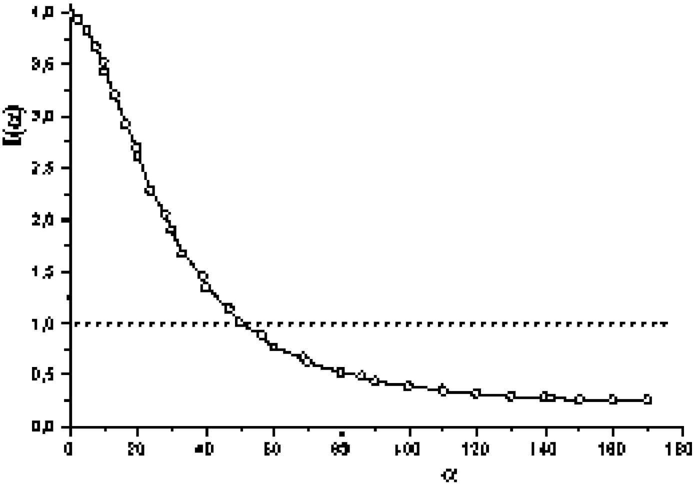
Strangely enough, the crude scheme presented on Figure 1c considerably wins in comparison with first two as it allows to create almost uniform illumination of all dilatometer surfaces. Calculation show, that the angular distribution received from this illumination scheme is close to a correct hexagon. Naturally, such distribution is not ideal, however, it allows to create almost identical intensity in the whole volume of the dilatometer with not absorbing solution.

Our experiments have allowed to offer the ideal scheme of illumination represented on Figure 1d. In this scheme a linear source of radiation and the dilatometer are on the common axis. Thus the dilatometer is located higher then a light source that it is convenient for its removing if it is necessary. Near to the light source L the conic



(a)

FIGURE 2 (a) Dependence of an angle α of a beam entering in the second focus of an ellipse from a angle of an exit φ from the first focus; (b) Dependence of irradiation intensity of the sample placed in the second focus, on an angle of a beam falling on cylindrical dilatometer.



(b)

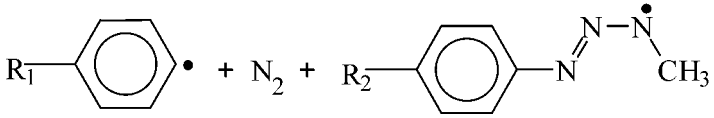
FIGURE 2 Continued.

mirror with an angle at the top of the cone, which is equal 90°. Thus, the light rays proceeding perpendicularly of a source axis are distributed by a parallel beam upwards. Near to the dilatometer one more the same conic mirror providing turns of beams aside the dilatometer is put. The double reflection of light is reduced to that on some distance from dilatometer in parallel an axis dilatometer as though there is a source allocated on a circle (on Fig. 1d shown by dashed lines). To exclude hit on the dilatometer the beams reflected from a mirror only once higher than a light source and lower than the dilatometer the round screens E which are not preventing beams, twice reflected from mirrors are put.

Thus, the scheme presented on Figure 1d, allows to illuminate a researched solution in regular intervals. The radial distribution of intensity of light getting on dilatometer will depend on diameter of a luminous column in a discharging lamp. If this diameter is much less than the diameter of the dilatometer it is possible to suggest, that that intensity of a falling light with a reduction of the distance up to an axis of the dilatometer will increase in the inverse proportion to distance. If a diameter of a luminous column in a lamp is not less then diameter of the dilatometer the intensity of a falling light will not depend on a distance inside the dilatometer.

RESULTS AND DISCUSSION

Pentazadienes-1,4 are shown [1,2] to be decomposed on some radicals and a molecule of nitrogen by photolysis:



i.e., intermediate products of pentazadiene (*Pz*) photolysis are aryl ($P_1^\bullet$) and triazene ($P_2^\bullet$) radicals, and also a molecule of nitrogen [3].

Photopolymerization kinetics of methymethacrylate was studied by the dilatometry method. Dimethylformamide is served as a solvent. The concentration of the photoinitiator is varied over the range of $1{\cdot}10^{-3} \div 3{\cdot}10^{-2}$ mol/l, and a monomer – 0,5 ÷ 2 mol/l. The irradiation of a solution was carried out by an integrated light of a mercury lamp of a high pressure in the glass cylindrical dilatometer which does not transmit a light with $\lambda < 320$ nm, i.e., it was absent a direct absorption of a light by a monomer and a solvent. As control experiments have shown, in an absence of photoinitiators in these conditions the photopolymerization does not carry out.

By studying of the reaction of methylmethacrylate polymerization at presence of pentazadienes I – III has been shown, that at the same concentration of a monomer velocity of polymerization is maximal in a case of pentazadiene **II** and minimal (close to zero) – for pentazadiene **III**, that perfectly correlates with values of quantum yields of pentazadiene photolysis (0,15 для **I**, 0,38 для **II**, 0,004 для **III**). If instead of pentazadiene as the initiator to use one of the effective known initiators - benzoine it appears that in the quartz dilatometer a speed of initiation of methylmethacrylate polymerization has the same order, as at use pentazadiene **II** in cylindrical dilatometer. Hence, pentazadienes are effective initiators of the polymerization (Fig. 3).

Reactions of photopolymerization proceeding in a solution are described with the help of the approximate scheme:

$$\mathrm{Pz} \xrightarrow{h\nu} \mathrm{P}_1^{\bullet} + \mathrm{P}_2^{\bullet} + \mathrm{N}_2 \tag{1}$$

$$\mathrm{P}_i^{\bullet} + \mathrm{M} \xrightarrow{k_i} \mathrm{P_iM}\bullet, \quad i = 1, 2. \tag{2}$$

$$\mathrm{P_iM} \bullet + \mathrm{M} \xrightarrow{k_3} \mathrm{P_iM}_2^{\bullet} \tag{3}$$

$$\mathrm{P_iM}_n^{\bullet} + \mathrm{M} \xrightarrow{k_3} \mathrm{P_iM}_{n+1}^{\bullet} \tag{4}$$

$$\mathrm{P_iM_n} \bullet + \mathrm{P_jM}_m^{\bullet} \xrightarrow{k_4} \mathrm{P_iM_{n+m}P_j}, \quad i, j = 1, 2. \tag{5}$$

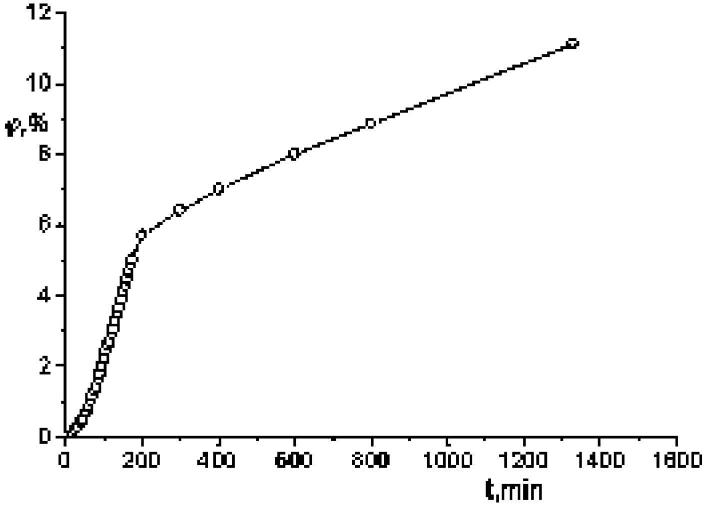


FIGURE 3 Kinetic curves of polymerization of 20% MMA (1) at the presence of the initiator (2 %).

$$\mathrm{P_iM_n^\bullet + Q \xrightarrow{k_5} \text{ПродуКТ}} \tag{6}$$

$$\mathrm{P_iM_n^\bullet + RH \xrightarrow{k_6} P_iM_nH + R\bullet} \tag{7}$$

$$\mathrm{P_iM_n^\bullet + R^\bullet \xrightarrow{k_7} P_iM_nR} \tag{8}$$

In this scheme it is considered that each of the formed radicals can initiate polymerization, but with different constants of velocities (accordingly k1 and k2). The further growth of a polymeric chain will proceed with the permanent speed (reactions 3 and 4). Reaction (5) is corresponded to square-law termination of polymerization, and a reaction (6)–(8)–to linear. Reactions (7) and (8) describe an interaction between macroradicals and molecules *(RH)* and radicals ($R\bullet$) of a solvent with the termination of a chain. In this connection the solvent radical most likely does not possess an initiating ability.

This scheme of processes allows to receive the solving for the sum of radicals $y = \sum_{i=1}^{2}\sum_{m=1}^{\infty}\left[P_iM_m^\bullet\right]$:

$$y = A\frac{th(Ak_4^2t) + \frac{B}{2Ak_4}}{1 + \frac{B}{2Ak_4}th(Ak_4^2t)} - \frac{B}{2k_4}$$

where

$$\beta = \frac{k_1M}{k_1M + k_{41}\sum\limits_{i,n}[P_iM_n^\bullet] + (k_{51}[Q] + [RH]\{k_{61} + k_{71}k_6/k_7\})}$$

$$+\frac{k_2M}{k_2M + k_{42}\sum\limits_{i,n}[P_iM_n^\bullet] + (k_{52}[Q] + [RH]\{k_{62} + k_{72}k_6/k_7\})},$$

$$A = \left(\frac{\beta\varepsilon\varphi[Pz]I(x)}{k_4} + \frac{(k_5[Q] + 2k_6[RH])^2}{4k_4^2}\right)^{1/2},$$

$$B = k_5[Q] + 2k_6[RH].$$

The stationary concentration of polymeric radicals can be found from the equation:

$$y_{cm} = \left(\frac{\beta\varepsilon\varphi[Pz]I(x)}{k_4} + \frac{(k_5[Q] + 2k_6[RH])^2}{4k_4^2}\right)^{1/2} - \frac{(k_5[Q] + 2k_6[RH])}{2k_4}.$$

In case of a weak efficiency of linear radicals suppression for stationary concentrations we can find

$$y_{cm} = \left(\frac{\beta\varepsilon\varphi[Pz]I(x)}{k_4}\right)^{1/2}.$$

Now the equation for polymerization of methylmethacrylate type can be found in the form:

$$\frac{dM}{dt} = -\beta\varepsilon\varphi[Pz]I(x) - k_3M\left(\frac{\beta\varepsilon\varphi[Pz]I(x)}{k_4}\right)^{1/2}.$$

The first part of the equation corresponding to an initiation is usually very small in comparison with the second part. Therefore it could be neglected.

And, at last, for a degree of monomer conversion we can obtain

$$\frac{1}{d}\int_0^d dx \int_0^t \frac{dM}{M} = -k_3\frac{1}{d}\int_0^d \int_0^t \left(\frac{\beta\varepsilon\varphi[Pz]I(x)}{k_4}\right)^{1/2} dtdx.$$

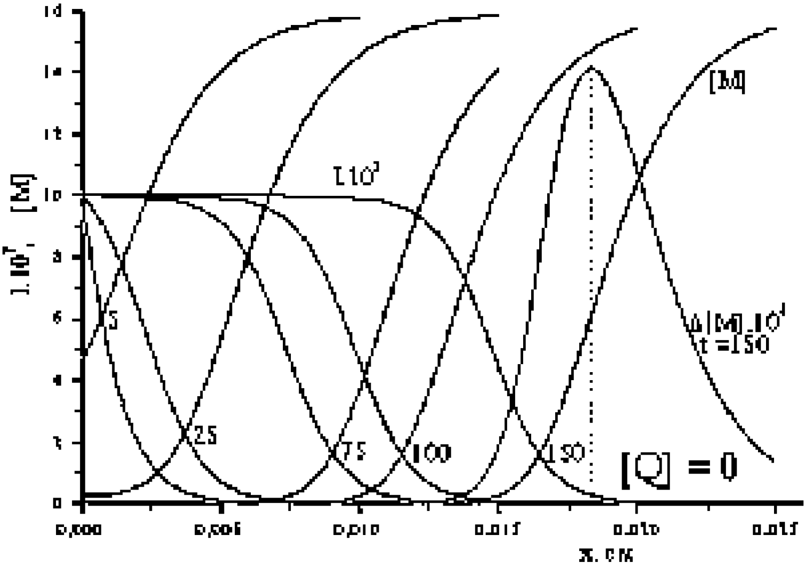


FIGURE 4 Disribution of light intensity (I), monomer concentration ([M]) and polymerization yields (△[M]) by dilatometer thickness at different irradiation times.

i.e., the degree of conversion does not depend on the concentration a monomer, if for parameter β such dependence is absent.

Experimental testing of the last equation has shown, that within the limits of experiment method errors of a dependence of the conversion value from a concentration of a monomer is practically absent.

For thick dilatometers is necessary to take into consideration, that

$$I(x) = I_0 \exp\left(-\int_0^x \varepsilon[Pz(x)]dx\right),$$

$$\frac{d[Pz(x)]}{dt} = -\varphi\varepsilon[Pz(x)]I(x).$$

For the decision of such problem it was necessary to take advantages of computers. By carrying out of calculations has been shown, that in this case a photochemical reaction proceeds in a narrow near-surface layer. With time in this layer pentazadiene disappears, and the front of reaction moves deeply into a solution (Fig. 4). Calculations show, that the front of a reaction goes with a permanent velocity. Hence, the established process of photopolymerization should be described as a linear function of time. The deviation from such dependence should be observed only in an initial stage when the front of reaction is only created. Such dependence we really observe (Fig. 4) in experiments.

From Figure 4 it follows, that at carrying out of computing experiment we simultaneously can fix a light intensity and quantum yields (length of a polymeric chain) of polymerizations. Hence, we can determine distribution of formed polymer on molecular weights.

CONCLUSIONS

1. Methods of volume photopolymerization studies are developeded and is shown, that the best design of irradiated cylindrical dilatometer with a photopolymerizable solution is such irradiator at which a source and dilatometer are located on one axis, and in radiation due to two conic mirrors passes into the dilatometer.
2. Photopolymerization kinetics at the big value of initiator optical density contains two components, one of which corresponds to polymerization at the dilatometer surface, and the second one – to reaction front movement deeply into the dilatometer.
3. Computer processing of photopolymerization kinetics results to study the molecular weights distribution of formed polymer.
4. During all polymerization kinetics distribution of polymeric molecules yield from polymeric chain length is kept permanent

REFERENCES

[1] Syromyatnikov, V. G., Kondratenko, N. P., Novikova, E. A., & Avramenko, L. F. (2003). *Polymer Science Series B*, *45*(1–2), 32.

[2] Kondratenko, N. P., Avramenko, L. F., Kondratenko, P. A., & Syromyatnikov, V. G. (2000). *Functional Materials*, *7*, 4(1), 613.

[3] Syromyatnikov, V. G., Kondratenko, P. A., Kolendo, A. Yu., Novikova, E. A., Paskal, L. P., Bezdushnaya, E. G., Yeshchenko, N. P., Prot, T., & Golec, K. *Russian Chemical Reviews*, in press.