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# **Segmented Polyurethane Elastomers for Endovascular Surgery: Kinetics, Properties, Application**

PhD Thesis

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## 1. Introduction

Arteriovenous diseases are extremely dangerous and threaten a large part of the population. A large number of premature deaths are caused by such diseases, and both their detection and treatment is often extremely difficult. These problems usually originate from the formation of aneurysms or arteriovenous malformations (vein tumors) in the blood vessels [1]. The walls of the vessels become weak at certain places and the burst of the veins may result in bleeding. Such malformations can form everywhere in the body, but they are extremely dangerous in the brain. 50 % of the patients who have a bleeding (stroke) do not survive, and even in the case of a successful treatment there is a high chance of permanent brain damage. The early way to prevent bleeding in these cases was open surgery, which was extremely dangerous and showed high mortality rate. Aneurism and arteriovenous malformations are treated more and more frequently by endovascular techniques. These methods, in which the treatment takes place directly in the blood vessel, show better results than micro-neurosurgical methods. Micro balloons and spirals are frequently applied [2], but liquid embolizing agents are the newest materials used for the treatment. These are less invasive than earlier methods and result in very high recovery ratios.

Although polymer based embolizing agents are available already on the open market, but they have numerous drawbacks, which hinder the more extensive spread of this approach. Intensive research is going on in the field as a consequence, and the improvement of existing solutions as well as finding completely new materials or approaches are equally interesting for the medical community. Medical doctors from the University of Pécs approached the Laboratory of Plastics and Rubber Technology to join their effort in finding a polymer with optimum properties for endovascular surgery. They did considerable research already and found that a certain polyurethane polymer performs much better than the commercial embolizing preparation based on an ethylene-vinyl alcohol copolymer. The polymer, which is a commercial product, is produced expressively for medical applications, but not for endovascular surgery. As a consequence, its properties are not optimal for the purpose, its characterization is insufficient, the production technology is not known, thus it cannot be certified as the component of a registered product for embolization. The discussions between the Laboratory and the doctors lead to a few preliminary experiments and finally to a large project financed by the National Bureau for Research and Development (NKTH).

1. Valtonen, S., *Operat. Tech. Neurosurg.* **3**, 231 (2000)

2. Guglielmi, G., *Operat. Tech. Neurosurg.* **3**, 191 (2000)

The first steps of the research were extremely difficult. Based on the information available, we tried to identify the chemical composition and structure of the polymer, characterized it as thoroughly as possible, explored various reaction routes and preparation technologies, developed methods for characterization, etc. During this preliminary stage we found that besides producing an appropriate polymer, we must pay attention also to the entire preparation, to the solution used for embolization. As it turned out, we had to look into contrasting methods and the factors affecting the stability of the suspension prepared with the selected contrast material [3]. Commercial contrast agents often separated from the suspension by sedimentation. Quite a few of these problems were completely new to us and we often failed to find the right solutions, wandered off the main path towards reaching our goal, sometimes even got completely stuck. This PhD thesis is one of the first products of this large project and it reports some of the results obtained up to now. The thesis might not seem to be completely coherent and the chapters focus on apparently different problems, but all of them represent a very important step toward the final goal. The components and the composition of the polyurethanes studied cover a wide range and we investigated various questions from polymerization kinetics, through structure-property correlations, to the problematic of contrasting. We hope that the work done and the compilation of the results in this thesis give a further boost to the project resulting in even better scientific results and a material, which finds widespread use in surgery.

Polyurethane synthesis is a polyaddition reaction, with the consequence that the degree of polymerization is very sensitive to the stoichiometric ratio of the two components. The chemical characteristics of the isocyanate groups are also extremely important. These groups are very reactive, especially with nucleophile agents like alcohols. The products of the primary reactions of isocyanate and alcohol or isocyanate and water still contain active hydrogen atoms, which can further react with isocyanates forming allophanates from urethanes, or biuret from carbamide. During the reaction of the isocyanate and alcohol electron is transferred between the carbon atom of the electrophile isocyanate and the nucleophile oxygen atom of the hydroxyl group, resulting in an intermediate complex, which then leads to the final urethane product. The literature on the structure of the complex is not unified, alcohol-alcohol, alcohol-urethane, isocyanate-alcohol and isocyanate-urethane complexes have been assumed [4]. The understanding of the kinetics of the particular polyurethane synthesis can provide better control over material properties.

3. Brinker, J., *Rev. Cardiovasc. Med.* **4**, S19 (2005)

4. Crawford, D. M., Bass, R. G., Haas, T. W., *Thermo. Acta* 323, 53 (1998)

Limited number of models is available for the description of the reaction kinetics of polyurethanes. The simplest is the  $n$ -th order model (Eq. 1), which can be used in those cases when the initial, maximum reaction rate decreases continuously with time.

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (1)$$

where  $\alpha$  is the conversion and  $k$  is the rate constant. If the measured reaction rates do not decrease continuously as a function of time, we must assume that reaction products influence the further course of polymerization, have catalytic effect on it. In such cases the autocatalytic model can be applied reasonably well. This model describes chemical processes in which the initial zero reaction rate increases as the reaction progresses. Several researchers found, that the urethane formed during polymerization has such catalytic effect. However, in the autocatalytic model the initial reaction rate is 0, which means that in itself cannot be used to describe real systems. As a consequence, this approach is usually combined with the  $n$ -th order model. The result is known in literature as the Kamal-Sourour equation [5] (Eq. 2).

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (2)$$

where  $m$ , and  $n$  are partial reaction orders. Although the Kamal-Sourour model describes most two-component polymerization reactions quite well if reaction orders are selected arbitrarily as non-integer numbers, the physical meaning of these constants is questionable. The equation developed by Sato (Eq. 3) offers a more rigorous approach by considering polyurethane synthesis as the combination of an alcohol and a urethane catalyzed process [6,7].

$$\frac{d\alpha}{dt} = (K'_1 + K'_2\alpha)(1 - \alpha)^2 \quad (3)$$

where  $k_1$  is the rate constant of the  $n$ -th order, while  $k_2$  that of the autocatalytic reaction. Diffusion control must be considered in melt polymerization for several reasons in the kinetic characterization of such systems. In such reactions, apart from the initial phase, the actual reaction rate is usually slower in the entire conversion scale than expected from chemical considerations. Additionally, the reaction does not proceed to 100 % conversion. Complementing any kinetic model with the Fournier equation in order to account for diffusion control provides more accurate results, since diffusion can have a rather large impact on the polymerization reaction.

5. Kamal, M. R., Pol. Eng. Sci. 13, No. 1, (1973)
6. Sato, M., J. Am. Chem. Soc. 82, 3893 (1960)
7. Sato, M., J. Org. Chem. 27, 819 (1962)

The properties of such materials are determined by the molecular structure. Almost independently of the type of PU, these polymers possess segmented structure. The soft segments, which are formed from high molecular weight polyols, are mobile and are normally present as coils, while the hard segments, which are formed from the isocyanate and the chain extender, are stiff and immobile. Because the hard segments are covalently coupled to the soft segments, they act as cross-links, and inhibit the plastic flow of the polymer chains thus creating elastomeric resiliency. Upon mechanical deformation, parts of the soft segments are stressed by uncoiling, and the hard segments align in the stress direction. This reorientation of the hard segments and the consequent powerful hydrogen bonding results in high tensile strength, elongation, and tear resistance. Hydrogen bonds and van der Waals interactions develop between the polymer chains. The segmented structure of the polyurethane chains leads to phase separation, which occurs because the mainly non-polar, low melting soft segments are incompatible with the polar, high melting hard segments. An increase in the chain length of the polyol results in an increased flexibility of the polymer chain and in a more elastomer like behavior. Polyurethanes containing short chain length polyols are stiffer materials with larger strength. However, the size, structure and properties of the actual hard and soft segments may vary in a wide range depending on the exact composition of the polymer chain. The separation of the two phases depends on the interaction between the polymer chains, and the developing phase structure determines mechanical properties. The soft and hard segments can organize into micro crystallites or fibrils.

Besides the properties of the polyurethane, also the characteristics of the entire embolizing preparatum must be considered during development. The embolization system must meet numerous requirements i.e.: low viscosity (the procedure is carried out in a 0.1 mm thick catheter); rapid filling of large aneurysms; quick precipitation, but not in the catheter; the precipitate should take the shape of the aneurysm; the material should be flexible; the preparatum must be able to be withdrawn into the catheter for a short period of time; no washing with DMSO should be required; stability against a turbulent blood stream should be exhibited; the catheter need to be easily removed from precipitate; and no sticking to wall of blood vessels must occur. A closer scrutiny clearly shows that most requirements can be fulfilled by the appropriate choice of the polymer. On the other hand, a number of properties are influenced by the contrast material and the solvent as well. The viscosity of the solution, for example depends on the choice of

all three components.

Radiocontrast agents are compounds used to improve the visibility of internal bodily structures in an X-ray image. The degree of contrast and the suitability of a material for surgical purposes depend on its electron density and on the stability of the suspension, which on the other hand, is determined by the particle size and density of the contrast agent and the viscosity of the dispersion. There are two basic types of contrast agents used in X-ray examinations. One is based on metals or metal salts like barium sulfate, which is an insoluble white powder. Several other contrast materials are also used in medical practice like, gold and tantalum. The other type of contrast agent is based on iodine. This may be bound either in an organic (non-ionic) compound or an ionic compound. Ionic agents were developed first and are still in widespread use depending on the examination they are required for. Ionic agents have a poorer side effect profile. Organic compounds have fewer side effects as they do not dissociate into component molecules. Currently iodine based radiocontrast materials are used for the examination of aneurysms, and tantalum based is used during treatment. However there are problems with the currently applied tantalum material. Although it has all the relevant approvals it does not always behaves optimally during treatment. The largest problem is that tantalum might sediment in the catheter clogging it. The phenomenon is very dangerous as high pressures are required to push the plug through, even if it is possible at all.

Both the chemistry and the structure-property correlations of segmented polyurethanes are extremely complicated. As a consequence, many questions are still open in spite of many decades of research and industrial application. Our task, the preparation of a polymer with optimum properties for endovascular surgery is further complicated by the stringent conditions and complex requirements of the application. The apparently diverse issues discussed in this thesis are connected by the same goal and drive the project towards its conclusion. Instead of randomly selecting interesting scientific problems, we had to carry out experiments oriented by the application and by the needs of our partners. In spite of the prominent role of practical questions in our research, we always drove for deeper understanding of the problems investigated in the hope that we can find correlations of general validity, which can help us in the further course of the project. Accordingly, this thesis addresses questions which have not been investigated up to now, or have not been answered satisfactorily yet. Most, but not all, of these issues are in line with our competence, but the entire thesis represents the opening of a new area for the Laboratory by focusing attention onto the medical application of polymers and within this huge area more specifically onto the

sensitive question of polymers used for endovascular surgery.

## 2. Experimental

Polyurethanes were prepared from 4,4'-methylenebis(phenyl isocyanate) (MDI), 1,4-butanediol chain extender (BD) and poly(tetrahydrofuran) polyether polyol with a molecular weight of 1000 (PTHF). For our kinetic study a polyester polyol was used instead of PTHF with the molecular weight of 2000 and average functionality of 2. MDI, PTHF and the chain extender were purchased from Aldrich. The commercially available polyol Lupraphen 8101 was supplied by Elastogran Kemipur Kft. Polymerization was carried out by melt reaction in an internal mixer (Brabender W 50 EH) at 150 °C, 50 rpm for 30 min. The polymer was compression molded into 1 mm plates at 200 °C and 5 min for characterization using a Fontijne SRA 100 machine.

Differential scanning calorimetry (DSC) was used for the study of polyurethane kinetics with a Perkin Elmer Diamond DSC instrument at 80, 90, 100, 110 and 120 °C under constant helium flow. Samples prepared for the structure-property study were characterized. Fourier transform infrared spectroscopy (FTIR), wide angle X-ray diffraction (XRD), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), gel permeation chromatography (GPC), mechanical testing and the determination of light transmission.

In the contrasting experiments of this study BaSO<sub>4</sub> particles were prepared from solution by mixing barium chloride (99.0 %, Spektrum 3D, Hungary) and sodium sulfate (99.5 %, Reanal, Hungary). The reagents were used as received. The reaction was carried out under various conditions; we changed the concentration of the solutions, reaction temperature, the order and way of mixing. Ethanol (96 %, Spektrum 3D, Hungary) was added to the suspension in order to prevent aging. The size of the particles was determined by scanning electron microscopy (SEM) and laser light scattering (LLS). 1 g material was suspended in 100 ml ethanol for SEM. One droplet was placed on a sample holder, the solvent was evaporated and the particles were coated with gold. Micrographs were taken with a JEOL JSM-6380 apparatus. Dynamic laser light scattering measurements were done using a Brookhaven BI 9000 apparatus at 90° scattering angle in ethanol and DMSO, the solvents used in endovascular surgery. The concentration of the suspension was 0.1 g/100 ml and the suspension was treated with ultrasound for 10 min before the measurement. The sedimentation of the particles was studied by recording the movement of the sedimentation front. 1 g material

was suspended in 10 ml solvent in a closed graduated cylinder and the sus-

pension was shaken vigorously for 5 min before the measurement. The movement of the sedimentation front was followed by a camera, visualized with the Vision GS software, recorded by Bulent's Screen Recorder and evaluated by the BSR Movie Lab software. Sedimentation was studied in water, ethanol and DMSO.

### 3. Summary

In recent years we obtained several indications that the interest of both the public and the scientific community turned much more towards bio-related materials and the medical application of polymers than before. Projects related to natural polymers were initiated by some companies, thus we carry out research on natural fibers, wood flour filled polymers and plasticized starch. We launched smaller or larger projects on the mechanical testing of tissues and knee joints, on the regeneration of bones or on the application of polyurethane for brain surgery. This last project was initiated upon the request of medical doctors, who actually use these materials in practice. The first, rather simple goal of the research was to reproduce the polymer applied presently and prepare one with similar or the same properties. However, new and more ambitious goals were defined as the research progressed and the project expanded. Besides producing tailor made polymers for the treatment of specific diseases, we hoped to generate both scientifically and practically relevant knowledge and solutions, which might be used in further research and development. This thesis is dedicated to the investigation of specific questions related to the preparation and use of segmented linear polyurethane elastomers for endovascular surgery. We focused attention on the kinetics of polymerization, on the characterization of structure and on structure-property correlations, i.e. on questions which traditionally constitute the strengths of the Laboratory. Although we summarized the most important results of the research at the end of each chapter, we briefly repeat them here to give a concise overview of our achievements.

The kinetic study carried out on three-component segmented polyurethane elastomers confirmed the assumption that melt polymerization is very complicated and it is affected by many factors. The results of the kinetic experiments could be analyzed relatively well by the Sato-Fournier model, while the simple  $n$ -th order and the Kamal-Sourour models failed in the studied system. Modeling proved that the relative weight of hydroxyl and urethane catalyzed reactions changes with composition. The lack of urethane catalysis in certain composition range was explained by the effect

of changing morphology, but the assumption must be proved with further experiments. Phase separation and changing  $T_g$  hindered reaching complete conversion at high butanediol contents, which justified the use of a term taking into account diffusion control. The analysis also showed that a side reaction, probably allophanate formation, also occurs at high butanediol content, which is not accounted for by the model used. The analysis of rate constants and activation energies proved that changing reaction rates result from concentration effects and not from the dissimilar reactivity of the diol components. The experimental and fitting procedure developed takes into consideration most of the factors affecting urethane polymerization and yield valuable information about the complex system studied.

In the next stage of the research results showed that changes in the NCO/OH ratio of segmented polyurethanes led to the expected changes in molecular weight. Other properties, however, did not depend only on molecular weight, and composition dependence showed apparent contradictions. Both strength and elongation-at-break increased with increasing isocyanate content up to the equimolar ratio of the two functional groups, but decreased only slightly at larger NCO/OH ratios, i.e. the correlations were asymmetric. On the other hand, modulus assumed a minimum value in the same composition range. By the analysis of various interactions developing in the polymer we developed a hypothesis which claims that phase separation plays an important role in the determination of properties. The interaction of chain-end  $-OH$  groups dominates at small NCO/OH ratio, while the interaction of hard segments at large isocyanate content. The extent of phase separation is the smallest and the number of mobile soft segments the largest at around the equimolar ratio of the two functional groups. While viscosity depends only on molecular weight, strength and deformability are strongly influenced also by interactions, which on the other hand drive phase separation and completely determine stiffness. Further experiments carried out to check the hypothesis completely confirmed its validity. We found that the strength of interaction determines properties at large isocyanate content, while molecular weight is the decisive factor at excess diol. The structure and properties of the phases forming at the two ends of the stoichiometric range differ considerably from each other.

In the last part of the research barium sulfate particles were prepared under various conditions to explore their potential application as contrast materials in endovascular surgery. The results showed that the particle characteristics of the samples depend very much on reaction conditions. Particles were obtained in spherical and plate-like shape and in a variety of

sizes. Primary particles of nanometer size formed aggregates in most cases.

Some of the samples had bimodal particle size distribution. Particle characteristics determined from SEM micrographs, by laser light scattering measurements and calculated from sedimentation experiments often differed from each other. The discrepancy could be explained by the different behavior of various fractions and by the dissimilar sensitivity of the measurements to them. Some of the samples showed various aging phenomena in DMSO leading either to the formation of larger particles or to the break down of aggregates. The experiments also proved that the appropriate selection of reaction conditions yield particles, which can be used for the preparation of stable suspensions. In the further course of the study we showed that the efficiency of solid particles used as contrast materials in endovascular surgery depends on their X-ray absorption capacity and on the stability of the suspension prepared from them. X-ray absorption is determined mainly by the real or effective atomic number of the element or compound used. The stability of the suspension prepared from the contrast materials is equally important. The sedimentation rate of particles depends on their size, on the density difference between the particles and the solvent, and on the viscosity of the medium. The particle characteristics and sedimentation behavior of the contrast materials studied covered a very wide range. The experiments proved that commercial contrast materials are not always ideal for the intended application and the appropriate selection of the contrast material yield stable suspensions, which safely can be used in endovascular surgery.

#### **4. New Scientific Results**

1. In a detailed kinetic study carried out on a three-component polyester polyurethane we proved that simple  $n$ -th order kinetics cannot describe the complicated mechanism of the polymerization. Hydroxyl and urethane catalysis takes place simultaneously and the actual weight of the two mechanisms changes with composition, with the ratio of the two diol components.
2. With the kinetic analysis of urethane polymerization we detected a side reaction in reaction mixtures containing large amounts of the butanediol chain extender. We assumed that this side reaction is the formation of allophanates caused by the large concentration of functional groups, the short chains of butanediol and by fast urethane catalyzed reactions. This latter assumption is proved by the fact that the relative intensity of the side reaction increases with temperature.

3. We developed a data processing and evaluation technique which facilitated considerably the testing of existing kinetic models. We showed that the only approach, which can be reasonably used for the analysis of our reaction system, is the Sato-Fournier model. The kinetic parameters derived from the model proved that the reactivity of the two diols used is similar and the large differences observed in reaction rates are caused mainly by concentration effects.
4. We established by the detailed study of structure-property correlations in polyether polyurethane elastomers that the two main factors determining properties are molecular weight and interactions. Different properties depend dissimilarly on the two factors; some are determined only by molecular weight, while interactions dominate for others. The strength of specific interactions are also important, molecular weight determines ultimate tensile properties at large  $-OH$  excess, while interactions are more important at larger isocyanate content.
5. We also pointed out that phase separation is driven by specific interactions in the studied polyether polyurethanes. However, besides the interaction of the urethane groups, the respective end-groups also interact with each other leading to a larger degree of phase separation and self-association within the phases. The properties of the phases differ considerably from each other as a consequence.
6. We prepared barium sulfate particles as potential contrast materials for endovascular surgery. We found that preparation conditions considerably change the shape and size of the particles. We observed that various aging phenomena may occur in DMSO suspensions of barium sulfate particles, they might dissociate or form larger aggregates considerably influencing their application as contrast materials.
7. We developed our own technique for the determination of the stability of contrasting suspensions. We could characterize most contrasting agents quite well with the method through the determination of sedimentation rate and sedimentation volume.
8. We proved that commercial contrast materials are delivered in a very wide range of particle sizes and shapes and the majority cannot be used as contrast agent in endovascular surgery, since the stability of the sus-

pension prepared from them is insufficient. The separation of the components by sedimentation may cause serious damage during surgery.

#### 4. Publications

##### 4.1. The thesis is based on the following papers

1. Pukánszky, B. Jr., Bagdi, K., Tóvölgyi Zs., Varga J., Dóczy T., Hudák I., Botz L., Pukánszky, B.: Polymerization Kinetics of Three-component Segmented Linear Polyurethane Elastomers: Effect of Composition, submitted to *Polymer*
2. Pukánszky, B. Jr., Bagdi, K., Tóvölgyi Zs., Varga J., Dóczy T., Hudák I., Botz L., Pukánszky, B.: Effect of Interactions, Molecular and Phase Structure on The Properties of Polyurethane Elastomers, accepted in *Progr. Colloid. Polym. Sci.*
3. Figyelmesei, Á., Pukánszky, B. Jr., Bagdi, K., Tóvölgyi, Zs., Varga, J., Dóczy, T., Hudák, I., Botz, L., Pukánszky, B.: Nanophase Separation in Segmented Polyurethane Elastomers; Effect of Specific Interactions on Structure and Properties, accepted in *Eur. Polym. J.*
4. Figyelmesei, Á., Pukánszky, B. Jr., Bagdi, K., Tóvölgyi, Zs., Varga, J., Dóczy, T., Hudák, I., Botz, L., Pukánszky, B.: Preparation and Characterization of Barium Sulfate Particles as Contrast Materials for Surgery, accepted in *Progr. Colloid. Polym. Sci.*
5. Figyelmesei, Á., Pukánszky, B. Jr., Bagdi, K., Tóvölgyi, Zs., Varga, J., Dóczy, T., Hudák, I., Botz, L., Pukánszky, B.: Contrast Materials for Endovascular Surgery: Efficiency and Characterization, submitted to *Neuroradiology*
6. Bagdi, K., Pukánszky, B. Jr.: Poliuretánok felhasználása érrendszeri betegségek gyógyítására, *Műanyag- és Gumiipari Évkönyv* 5, 73 (2007)

##### 4.2. Other Publications

1. Rácz, L., Pukánszky, B. Jr, Pozsgay, A., Pukánszky, B.: PA6/Montmorillonite Nanocomposites: Effect of Interaction on Structure and Proper-

ties, *Progr. Colloid. Polym. Sci.* **125**, 96-102 (2004)

2. Százdi, L., Pukánszky, B. Jr., Földes, E., Pukánszky, B.: Possible mechanism of interaction among the components in MAPP modified layered silicate PP nanocomposites, *Polymer* **46**, 8001-8010 (2005)
3. Százdi, L., Ábrányi, Á., Pukánszky, B. Jr., Vancsó, Gy., Pukánszky, B.: Morphology Characterization of PP/Clay Nanocomposites Across the Length Scales of the Structural Architecture, *Macromol. Mater. Eng.* **291**, 858-868 (2006)
4. Ábrányi, Á., Százdi, L., Pukánszky, B. Jr., Vancsó, Gy., Pukánszky, B.: Formation and Detection of Clay Network Structure in Polypropylene/Layered Silicate Nanocomposites, *Macromol. Rapid. Commun.* **27**, 132-135 (2006)
5. Százdi, L., Pukánszky, B. Jr., Vancso, G. J., Pukánszky, B.: Quantitative estimation of the reinforcing effect of layered silicates in PP nanocomposites, *Polymer* **47**, 4638-4648 (2006)
6. Dominkovics, Z., Renner, K., Pukánszky, B. Jr., Pukánszky, B.: Quantitative characterization of the structure of PP/layered silicate nanocomposites at various length scales, *Macromol. Symp.* in print

#### 4.3. Conference presentations

1. Pukánszky, B. Jr., Százdi, L., Ábrányi, Á.: Multiscale structure of Montmorillonite/PP nanocomposites, *Hungarian Nanotechnology Symposium 2005*, March 21-22, 2005, Budapest
2. Százdi, L., Pukánszky, B. Jr., Pukánszky, B.: Quantitative estimation of the reinforcing effect of layered silicates in PP nanocomposites, *IIMM 2005 Conference*, September 12-14, 2005, Lyon, France
3. Bagdi, K., Pukánszky, B. Jr., Pukánszky, B.: Poliuretán neuro-endovascularis em-bolizáló anyag fejlesztése, *Gyógyszerkutató szimpózium*,

November 24, 2006, Debrecen

4. Bagdi, K., Pukánszky, B. Jr., Pukánszky, B.: Poliuretán neuro-endovascularis embolizáló anyag fejlesztése – kémiai vonatkozások, *Gyógyszerkutatói szimpózium*, November 24, 2006, Debrecen (poster)
5. Dóczy, T., Hudák I., Botz, L., Pukánszky, B. Jr., Bagdi, K., Pukánszky, B.: Poliuretán alapú készítmények fejlesztése érrendszeri üregek kitöltésére vagy keringésből történő kiiktatására, *Congressus Pharmaceuticus Hungaricus XIII*, May 25, 2006, Budapest
6. Bagdi, K., Pukánszky, B. Jr., Pukánszky, B., Dóczy, T., Hudák, I., Botz, L.: Poliuretán alapú készítmények fejlesztése érrendszeri üregek kitöltésére vagy keringésből történő kiiktatására – kémiai vonatkozások, *Congressus Pharmaceuticus Hungaricus XIII*, May 25, 2006, Budapest (poster)
7. Pukánszky, B. Jr., Bagdi K., Pukánszky, B., Dóczy, T., Hudák, I., Botz, L.: Poliuretán (PU) alapú készítmények fejlesztése vertebroplasztika céljaira – kémiai vonatkozások, *Congressus Pharmaceuticus Hungaricus XIII*, May 25, 2006, Budapest (poster)
8. Pukánszky, B. Jr.: Több szintű szerkezet PP/Montmorillonit nanokompozitokban, *BME Doktoráns Konferencia*, February 7, 2006, Budapest
9. Bagdi, K., Pukánszky, B. Jr., Pukánszky, B.: Érrendszeri betegségek embolizációs gyógyítása poliuretánnal, *VII. Téli Iskola*, January 27, 2007, Balatonfüred
10. Pukánszky, B. Jr., Bagdi, K., Pukánszky, B.: Érrendszeri betegségek embolizációs gyógyítása poliuretánnal, *VII. Téli Iskola*, January 27, 2007, Balatonfüred
11. Bagdi, K., Pukánszky, B.: Poliuretán Neuro-endovascularis embolizáló anyag fejlesztése - Előállítás és szerkezet-tulajdonság összefüggések, *BME Doktoráns Konferencia*, February 7, 2007, Budapest
12. Pukánszky, B. Jr., Bagdi, K., Pukánszky, B.: Poliuretán Neuro-endovascularis embolizáló anyag fejlesztése - Az alapanyag készítménnyé fe-

fejlesztése, *BME Doktoráns Konferencia*, February 7, 2007, Budapest

13. Szőke, I., Bagdi, K., Pukánszky, B. Jr., Pukánszky, B.: Poliuretán elasztomer fejlesztése agyérrendszeri betegségek gyógyítása céljából, *Jubileumi Vegyész Konferencia*, May 29, 2007, Sopron
  
14. Bagdi K., Pukánszky B. Jr., Pukánszky B.: Structure property relationships in three component TPU elastomers, *VIII. COST Meeting*, September 12, 2007, Graz (poster)
  
15. Pukanszky B. Jr., Bagdi K., Pukánszky B.: Treatment of cardiovascular diseases with TPU based elastomers, *VIII. COST Meeting*, September 12, 2007, Graz
  
16. Bagdi K., Pukánszky B. Jr., Pukánszky B.: Structure property relationships in three component TPU elastomers, *9th Conference of Colloid Chemistry*, October 03, 2007, Siófok (poster)
  
17. Pukanszky B. Jr., Figyelmesi Á., Bagdi K., Pukánszky B.: Treatment of cardiovascular diseases with TPU based elastomers – with special regards to contrast, *9th Conference of Colloid Chemistry*, October 3, 2007, Siófok (poster)