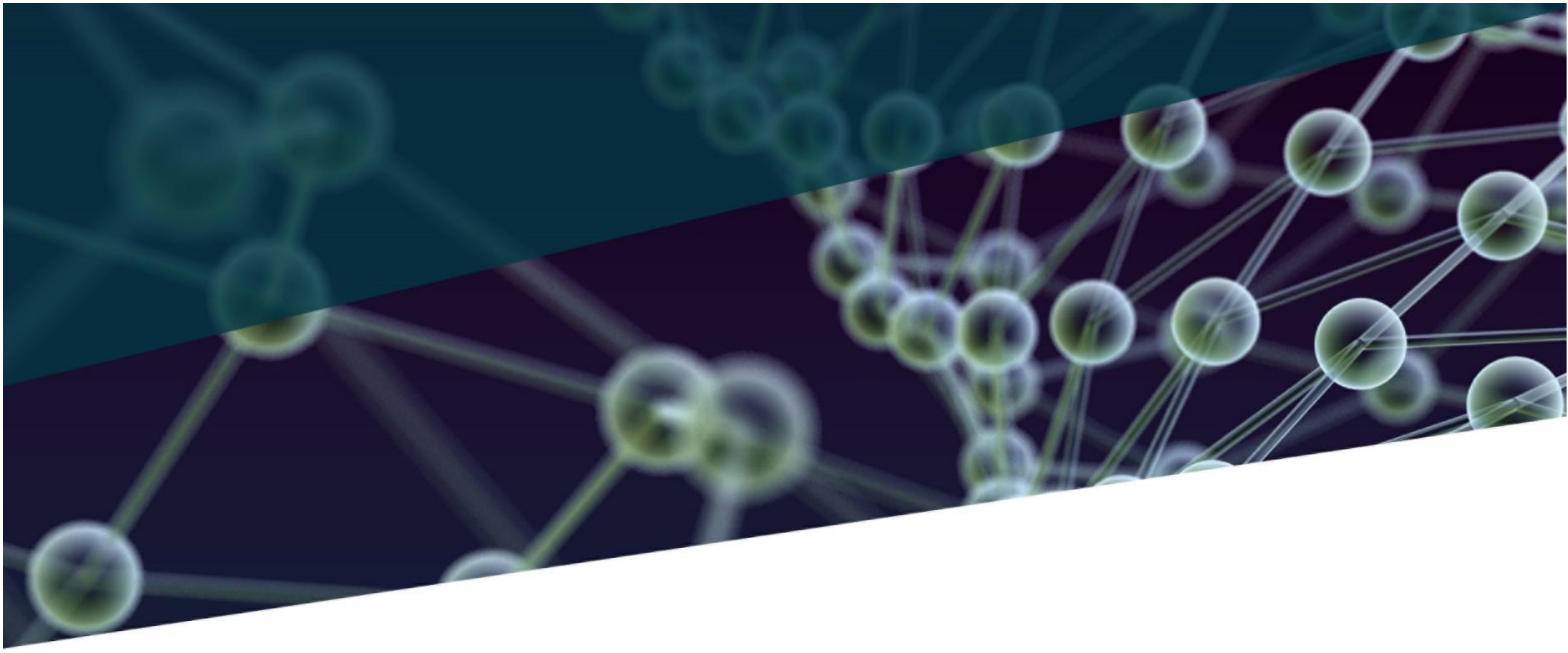
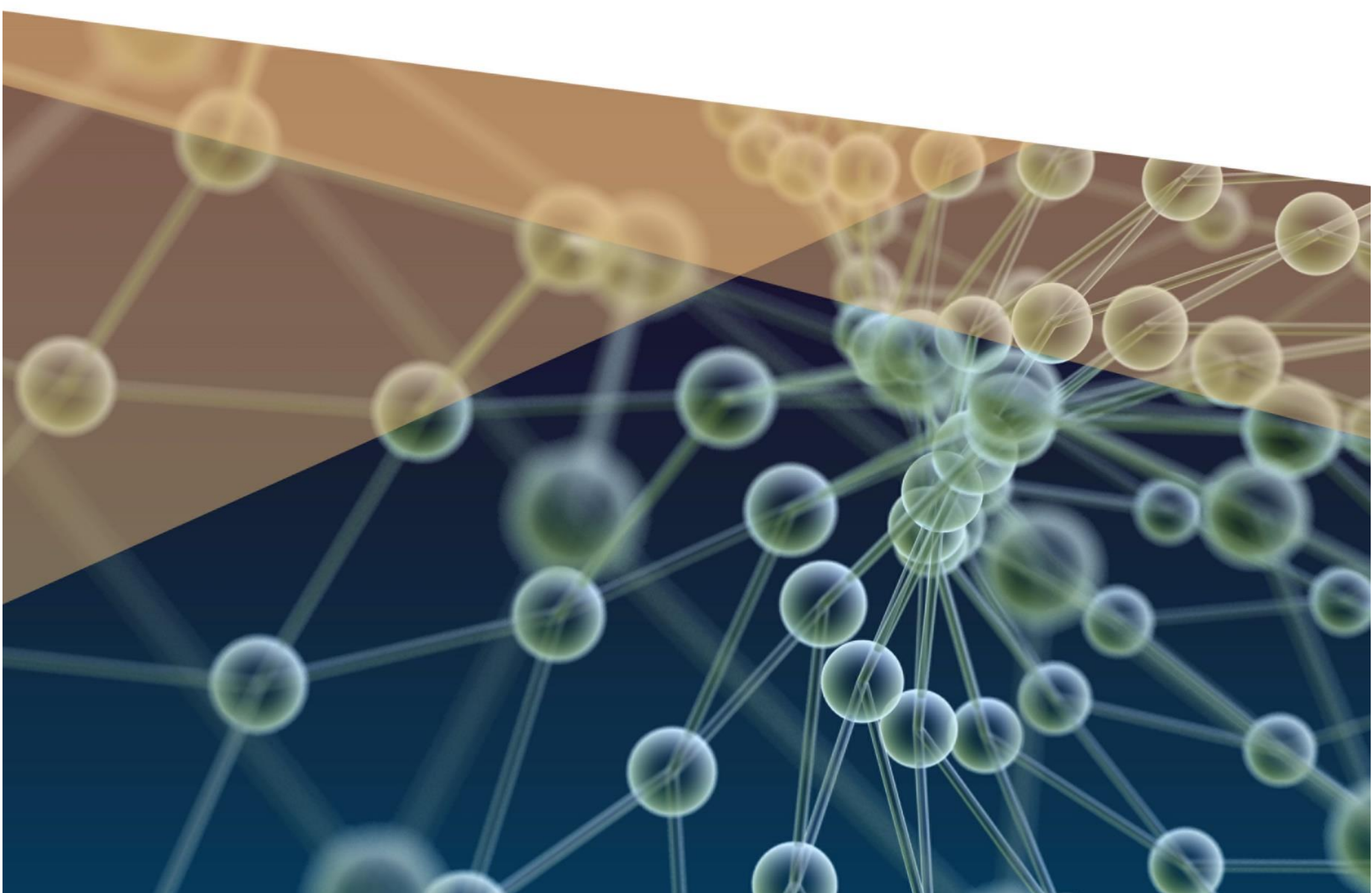


# Advanced Polymer Materials and Technologies

## Recent Trends and Current Priorities



Ministry of Education and Science of Ukraine
Kyiv National University of Technology and Design
Lviv Polytechnic National University

# Advanced polymer materials and technologies: recent trends and current priorities

# Перспективні полімерні матеріали та технології: останні тенденції та актуальні пріоритети

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The monograph contains the materials of the 4th International Conference "Advanced Polymer Materials and Technologies", which was held on October 11, 2022 at the Kyiv National University of Technology and Design together with the Lviv Polytechnic National University. The monograph deals with the creation of new polymer composite materials and their processing technologies using extrusion, electroforming, 3D printing, and other methods; development of environmentally-oriented technologies and equipment for the production of polymeric materials for various purposes, including biodegradable ones. Considerable attention is paid to the creation of new polymer composite materials, in particular for environmental protection, using waste from the chemical industry.

The monograph will be useful for teachers, students and graduate students, scientists and manufacturers whose activities are related to the above mentioned topics.

*The authors are responsible for the content of the publications.*

## CONTENTS

# NEW ACRYLATE POLYMERS – BASIS OF PAINTS FOR DRAWING ON WATER VIA USING EBRU TECHNOLOGY

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One of the important applications is their use in the production of daylight fluorescent pigments (DFP) and, based on them, enamel, decorative and polygraphic daylight fluorescent paints, and some polymeric materials (polyethylene, polypropylene, polyvinyl chloride, etc.). Pigments based on melamine-toluene sulfonamide-formaldehyde polymer (MTSF polymer) have found the most widespread usage. However, the dispersity of such pigment limits its possibilities when implemented in some directions. We developed pigments by emulsion polymerizing acrylic monomers with a particle size of 0.5-1 micrometers. Via the usage of organic luminophores, a color spectrum of emulsion DFP has been developed. The granulometric composition of pigments and their colorimetric characteristics (color tone, brightness, color purity) were studied.

**Introduction.** Synthetic polymers are widely obtained by processing low-molecular raw materials (phenol, formaldehyde, styrol, vinyl chloride, acryl).

Currently, polymers are used in almost all areas of production. They are used to make toys and building materials, implants, fabrics, medicines, lubricants for manufacturing machines, optical glasses, awnings and windows, furniture fabrics and fillers, packaging materials, advertising articles, artificial and synthetic fibers, films for various purposes, constructional materials, materials for electrotechnical and radio engineering industry, decorations.

In the production of consumer goods, it is of interest to obtain colored synthetic polymers (urea-, amino- and melamine-formaldehyde, polyester, and acrylate polymers) with a small molecular weight. Such oligomers are widely used for product decoration and new design solutions. To a greater extent, this applies to obtaining oligomers with luminescent properties. Such oligomers are called daylight fluorescent pigments. One of the essential applications of daylight fluorescent pigments (DFP) is enamel, decorative and polygraphic daylight fluorescent paints (DFF) obtained from them [1]. Due to their high brightness, these pigments and paints are used in cases where it is necessary to increase expressiveness and range of vision. They are widely used in civil aviation for coloring airplanes and airfield signs to improve flights in complex meteorological conditions. They color river and railway signs and are used in advertising, theatrical and decorative painting, and printing. The usage of daylight fluorescent pigments for manufacturing fluorescent pencils, paints, inks, etc., is well-known [2, 3]. In connection with the expansion of plastic fields of application, the role of aesthetic indicators of these materials, particularly the color and brightness of colors, has increased.

One of the interesting applications of such pigments is their use in developing paints for drawing on water using EBRU technology. This technology allows the application of exclusive designs on paper, fabrics, leather, etc.

This work aims to develop daylight fluorescent pigments on a formaldehyde-free basis with increased colorimetric characteristics and dispersity.

**Discussion.** Drawing on the water is a technology that allows you to create fantastic bright colors, which effectively flow into each other.

According to the EBRU technology, drawing on water means that the surface for applying the pattern is a liquid. However, this is not ordinary water, and the paint must be special.

EBRU is one of the types of ancient turkic-islamic art, first memories of it date back to the 12th century. The essence of this art type is the interaction of two liquids with a different consistency. Water with dissolved Hevea extract is poured into the container, and the water becomes thick. Also, painting involves using special paints containing ox bile and mineral dyes -- such paints are fluid enough to be decorative and beautifully spread over the surface. Only natural dyes have been used for centuries to produce original EBRU paints, obtained from colored rocks and earth, containing insolubly oxidized or organic pigments.

Using inorganic and natural pigments for production scaling up is unwise from a technological point of view. Therefore, much attention has recently been paid to developing organic pigments [4]. Such a way is used nowadays for murmuring not only paper but also leather, glass, wood, textiles, plastics, and other materials. The usage of daylight fluorescent pigments for such paints will expand their range.

One of the leading polymer or oligomer bases is amino formaldehyde, which can be modified with various components: polyester, polyamide, etc.

According to the data of the leading countries developing such materials (Great Britain, Japan, USA, Germany, etc.), pigments based on amino formaldehyde oligomers received the most widespread implementation.

Chemical connection of luminophore-polymer matrix significantly affects on pigments usage for obtaining DFF (at the same time, pigment's resistance to the action of organic solvents increases); affects on dyeing of polymeric materials, in particular polyethylene, polypropylene, polyvinylchloride (in this case, dyes migration resistance increase) and affects on some other applications.

Based on literature data, in the case of usage as a luminescent component of the compound with an active amino group, following the structure of the main structural link of MTSF-oligomer (Fig. 1) was proposed when using amino group-containing luminophores.

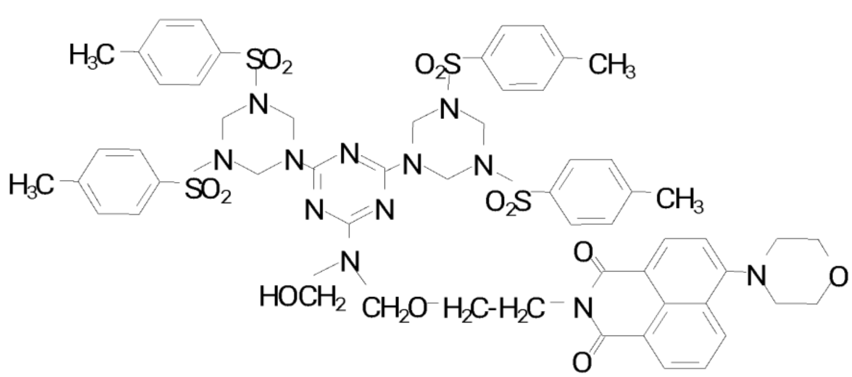



***Fig.1.*** *Structure of MTSF-oligomer main structural link with using 4-morpholino-N-(β-oxyethyl)naphthalimide*

Even though the resulting pigment has high physicochemical and colorimetric properties, it turned out to be unsuitable for creating paints for drawing on water.

The particle size of such a pigment is 5-10 micrometers. This is manifested in the form of inclusions in the figure.

Suppose melamine-formaldehyde polymers production is based on polycondensation principles, in which dye exhibits its maximum properties due to its entry into macromolecule structure. In that case, organic luminophore solubility in monomer plays an important role in polymerization pigments production.

The most effective luminescent components in the production of pigments based on several bases (melamine-formaldehyde, polyester, etc.) are derivatives of 4-morpholinonaphthalic acid [5].

Even though these derivatives have good colorimetric characteristics, some disadvantages limit the possibility of their usage in acrylate-based pigment development. One of them is the low solubility of some derivatives in monomers, in our case, in methyl methacrylate. In this regard, it was necessary to research corresponding analogs of 4-morpholinonaphthalimides. Figures 2-4 show the structural formulas of such compounds.

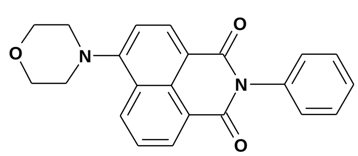


***Fig.2.*** *4-Morpholino-N-phenylnaphthalimide naphthalimide*

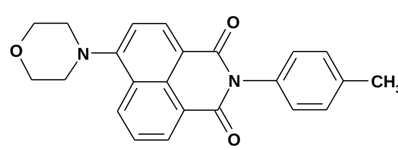


***Fig.3.*** *4-Morpholino-N-(n-methyl)-phenyl -naphthalimide*

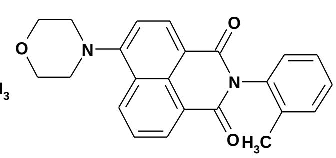
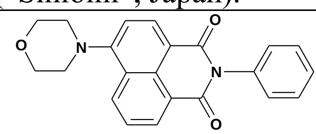
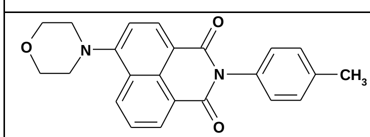
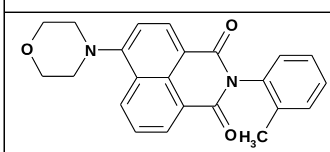


***Fig.4.*** *4-Morpholino-N-(o-methyl) phenyl*

Compounds 2 and 3 were not quite suitable for their usage as luminescent components of acrylate pigments due to their insufficient solubility in methylmethacrylate (solubility in the monomer is about 2% of the total mass). Color will not be saturated with the such value of concentration.

At the same time, 4-morpholino-N-(o-methyl)-phenylnaphthalimide dissolves in methylmethacrylate in the amount of 6 % from monomer weight at a polymerization temperature $80^0$C, because the molecule becomes less planar. Using these luminophores in the development of DFP made it possible to create pigments and enamels based on them with a color tone close to DFP, based on FANK (Table 1).

***Table 1**. Colorimetric characteristics of DFP based on synthesized organic luminophores*

| Luminophores | B, % | P, % | λ, nm |
|---|---|---|---|
| Lunar yellow LMP-series (“Swada”, Great Britain) | 122 | 87 | 567 |
| Lunar yellow FZ-series (“Sinloihi”, Japan). | 134 | 89 | 567 |
|  | 121 | 95 | 571 |
|  | 124 | 97 | 570 |
|  | 128 | 97 | 567 |

As can be seen from Table 1, when using 4-morpholino-N-(o-methyl)-phenylnaphthalimide, yellow pigment overruns the relative brightness of foreign analogs by 10-20%.  At the same time, particle sizes of yellow acrylate pigment obtained by us, were determined (Figure 5). For this purpose, pigment particles were dispersed in distilled water containing 0.001 % of the "neon" detergent.

A thin dispersion layer is applied to NaCl single-crystal fresh-pricked pattern. After that, a carbon replica is sputtered in a vacuum under $10^{-4}$ torr. The replica is separated in distilled water and air-dried. Studying and photographing were carried out on an EM-125 electron microscope under an accelerating voltage of 75 kV.

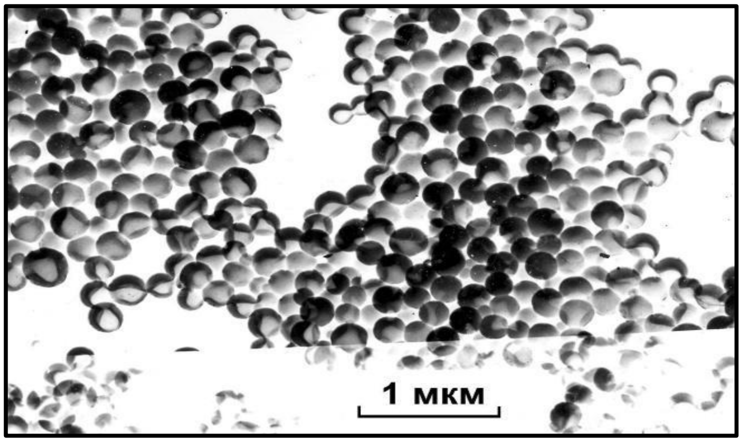



***Fig.5***. *Photomicrograph of yellow pigment on an acrylate basis*

As can be seen from Figure 5, particle sizes of obtained pigments are within 0.1-0.2 micrometers. This fact makes it possible to expand the fields of their use.

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# Перспективні полімерні матеріали та технології: останні тенденції та актуальні пріоритети

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