

Synthesis and properties of azidoaryl derivatives of cellulose

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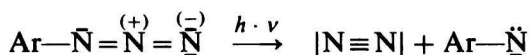
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Azidoaryl derivatives of hydroxypropyl- and hydroxyethylcellulose were synthesized by indirect method, modifying the polymeric chain by nitroaryl chromophores from which after reduction to amines, azides were prepared by reacting polymeric diazonium salt with sodium azide. Properties of the arising azides depend on the used polymeric substrate and on condensation reaction. Properties of soluble azido derivatives are characterized by gel permeation chromatography, thermal analysis, and UV and IR spectroscopy. In soluble derivatives photochemical efficacy in solid phase was tested.

Синтезировались азидоарилпроизводные гидроксипропил- и гидроксипропилцеллюлозы непрямым методом модификацией полимерной цепи нитроарильными хромофорами, из которых после редукции в амины приготовились азиды реакцией полимерной диазонионой соли с азидом натрия. Свойства приготовленных азидов зависят от употребленного полимерного субстрата и от употребленной конденсационной реакции. Свойства растворимых азидопроизводных описанные методом гелевой пермеационной хроматографии, методом термического анализа, ультрафиолетовой и инфракрасной спектроскопией. Испытывалась тоже фотохимическая эффективность растворимого производного в твердой фазе.

In recent years much attention was paid to research of systems capable to register information carried over by actinic radiation. Systems with such capability absorb impinging radiation and undergo photochemical changes narrowly connected with changes of their physicochemical properties. Property changes in irradiated points enable differentiation, by various methods, of the exposed and unexposed areas and visualization of the transferred information. Special attention among photosensitive materials is given to aromatic azides. In photochemistry of aromatic azides, high reactivity of nitrene as the primary intermediate of azido group photolysis is utilized [1]



Depending on the energetic state of the excited nitrene, it might be added to double bonds, might enter N—H and O—H bonds or might split off hydrogen from C—H bonds. In case that the mentioned photochemical reactions take place in polymeric films, they cause a change of their solubility brought about either by isomerization of the functional groups, or by crosslinkage of polymeric chains.

Photochemical properties of aromatic azides may be used for enzyme immobilization as well [2], which owing to nonstereospecific nitrene reaction partially lose catalytic activity for covalent linkage with polymeric carrier. It is known that this loss is much smaller than with other chemical immobilization methods.

This is the reason why photoimmobilized enzymes were proposed also for optical information recording [3]. By this method of information recording, the enzyme is photochemically immobilized by covalent bondage to the polymeric chain containing azidoaryl chromophores and after washout of the free enzyme the latent image is intensified by substrate solution; whereby the catalytic effect of the bound enzyme brings about the coloured matter. Mainly cellulose materials are used as polymeric carriers. The amount of the bound enzyme depends on the corresponding degree of substitution of cellulose chain.

In this paper synthesis of *O*-(4-azidobenzoyl)-*O*-hydroxypropylcellulose (*I*) and *O*-(4-azidobenzylidene)-*O*-hydroxyethylcellulose (*II*) and their properties are described. An indirect method of synthesis was chosen to achieve a high degree of substitution. Synthesis was realized by 4-nitrobenzoyl chloride and 4-nitrobenzaldehyde condensations to cellulose ethers and by consequent nitro group reduction. The polymeric azide was prepared by reacting diazonium salt with sodium azide.

Experimental

For synthesis 2-hydroxypropylcellulose (HPC) Klucel G (Hercules), $MS = 3.0$, $(M_r)_w = 3 \times 10^5$ ($DP = 892$) and hydroxyethylcellulose (HEC), Natrosol 250-GR (Hercules), $MS = 2.5$ ($DP = 352$) were used.

Electronic absorption spectra were measured by spectrophotometer Specord UV VIS (Zeiss, Jena). The infrared spectra were measured by spectrophotometer Perkin—Elmer (Mode 180, USA) in KBr tablets.

Molecular mass distribution changes in samples were studied by gel permeation chromatography in water and water—acetone media in a 60 cm \times 0.76 cm Sephadex G-15 column (Waters) registering the refraction index by differential refractometer (ALC-GPC 501). The eluent flow rate was 0.76 cm³ min⁻¹. Sample solution, mass fractions 0.2 % were dosed by a 2 cm³ loop.

Thermal stability of the synthesized materials was studied by thermal analysis (DTA) and thermal gravimetry (TG) by means of Thermoanalyser 2 (Metler, Switzerland) in an

inert nitrogen atmosphere with flow rate of $116.66 \text{ cm}^3 \text{ min}^{-1}$ and a thermal program of $6.0^\circ\text{C min}^{-1}$. For DTA, Pt—Pt, Rh thermocouples and freshly annealed Al_2O_3 as standard were used. For analyses 5.0—7.0 mg samples were weighed.

The photochemical activity of the prepared derivatives was verified by irradiation of the solutions and polymeric films by a medium-pressure mercury vapour lamp. Intensity of γ -luminous flux was $1.88 \times 10^9 \text{ e cm}^{-2} \text{ s}^{-1}$. Exposed samples were cooled by air circulation. Temperature at the level of impinging radiation was $21\text{—}22^\circ\text{C}$. Gel content in irradiated polymeric films was rated by weighing the insoluble portion after perfect water extraction (48 h).

O-(4-Azidobenzoyl)-*O*-hydroxypropylcellulose (I)

Hydroxypropylcellulose (8.0 g) was dissolved in 400 cm^3 of pyridine and 16 g (0.086 mol) of 4-nitrobenzoyl chloride dissolved in 50 cm^3 of benzene was added. The reaction took place in nitrogen atmosphere with a 3 h reflux. After reaction was completed, the product was precipitated by toluene, washed and dried *in vacuo*. The yield was 8.2 g of a light-yellow product (w_i (found): 54.50 % C, 7.07 % H, 36.33 % O, 2.20 % N).

To suspension of 0.41 g (0.01 mol) of reduction complex NaBH_2S_3 [4] in 50 cm^3 of tetrahydrofuran, 1 g of *O*-(4-nitrobenzoyl)-*O*-hydroxypropylcellulose was added. Reduction took place for 4 h under reflux and during this process the arising amino derivative fell out of solution. The product after reaction completion was separated, washed with water, ethanol and dried. The yield was 0.89 g (w_i (found): 40.76 % C, 4.86 % H, 53.02 % O, 1.36 % N).

Hydroxypropylcellulose diazonium salt was prepared according to [5].

To 0.75 g of hydroxypropylcellulose diazonium salt 0.6 g (0.009 mol) of sodium azide in 40 cm^3 of water was gradually added. The reaction took place in heterogeneous phase at $0\text{—}5^\circ\text{C}$ in $\text{H}_2\text{O}\text{—HCl}$ (mass ratio = 1 : 1) for 2 h. After completing of sodium azide addition the product was sucked off, washed in ethanol and vacuum dried. The yield was 0.71 g (w_i (found): 5.38 % N).

O-(4-Azidobenzylidene)-*O*-hydroxyethylcellulose (II)

O-(4-Diazoniumbenzylidene)-*O*-hydroxyethylcellulose chloride was prepared according to [6, 7]. Product II was prepared by the same way as the above-mentioned *O*-(4-azidobenzoyl)-*O*-hydroxypropylcellulose. (w_i (found): 18.9 % C, 2.45 % H, 2.40 % N).

Results and discussion

Synthesis of polymeric aryl azide by an indirect method was based on condensation reaction on 4-nitrobenzaldehyde and of 4-nitrobenzoyl chloride with polymeric cellulose substrate [6, 7]. The polymeric azide was prepared after

nitro group reduction to amino derivative by reacting sodium azide with polymeric diazonium salt derived from corresponding amino derivative. For modification we chose 2-hydroxypropylcellulose soluble in numerous organic solvents and water as well. Water-soluble hydroxyethylcellulose was condensed by nitrobenzaldehyde, while HPC was modified by nitrobenzoylization. The original HPC solubility in organic solvents and water was preserved only at lower degrees of substitution of nitrobenzoyl groups, whereby approximately from DS of NO_2 40—45 nitrobenzoyled HPC preserved its solubility only in dimethylformamide. On second synthesis grade, the nitro groups were selectively reduced to amino groups. *Campbell, Luescher, and Lerman* [5] used for nitrobenzoylcellulose reduction sodium dithionite, *Simionescu and Dumitru* [7] reduced nitrobenzoyl- and nitrobenzylcellulose by titanium chloride. *Sun', Derevitskaya, and Rogovin* [8] used for 4-nitrobenzoylcellulose reduction vanadium sulfate. Applying such processes for *O*-(4-nitrobenzoyl)-*O*-hydroxypropylcellulose reduction, the nitro group reduction was not quantitative, which might be caused by reduction in heterogeneous phase. Not even elongation of reaction time using sodium dithionite increased reduction efficacy, but on the contrary, the amino group content decreased. Looking for a suitable reduction agent, we concentrated on finding one selectively reducing nitro groups in heterogeneous phase. According to literature data complex dihydrogen sodium boric sulfide NaBH_2S_3 [9] possesses high reductive efficacy. The complex is highly selective for nitro group reduction. But not even this reduction agent for *O*-(4-nitrobenzoyl)-*O*-hydroxypropylcellulose in heterogeneous phase was able to achieve complete conversion. The efficacy was 75—80 % of nitro group reduction. Solubility of amino derivatives was very low and their swelling in ethanol, chloroform, and dimethylformamide only partial. Preparation of polymeric azide was carried out by nucleophilic substitution of diazonium salt by sodium azide. The reaction took place in heterogeneous phase in water-alcoholic medium. For *O*-(4-azido-benzoyl)-*O*-hydroxypropylcellulose similarly as for the amino derivative, a suitable solvent was not found. Different results concerning solubility compared with HPC derivatives were observed with condensation of 4-nitrobenzaldehyde and water-soluble HEC. HEC condensed by 4-nitrobenzaldehyde completely lost water solubility, but became soluble in organic solvents as acetone, chloroform, and dimethylformamide.

With regard to results of HPC nitro derivative reduction, we used in this case only sodium dithionite, known as very effective reduction agent [5]. Reduction brought about a change of the derivative solubility, whereby the amino derivative at the appropriate degree of substitution was fairly well soluble in water and ethanol, too. Preparation of polymeric azide was identical as that of HPC derivative. The resulting azido derivative was well soluble only in water (Table 1).

Table 1

Properties of synthesized azidoaryl derivatives of HPC and HEC

Product	$\lambda_{\max}/\text{nm}^a$	$\tilde{\nu}(\text{N}_3)/\text{cm}^{-1}$	$\text{DS}(\text{N}_3)^b$	Solubility
<i>I</i>	273	2124 680	52	Swells in ethanol
<i>II</i>	268	2100 680	18	Water, DMF, in ethanol swells substantially

a) Measured in ethanol; *b*) total degree of substitution (DS) calculated from elemental analysis.

Process of synthesis in this case was followed by means of gel permeation analysis. Fig. 1 illustrates elution curves of the individual products. The elution curves demonstrate that the used HEC (curve 1) represents a polymeric system with a comparatively narrow molecular mass distribution. Preparation conditions of the aromatic nitro derivative, especially the rather acid medium, caused a considerable HEC degradation. Loss of the high-molecular portion represents about 50 mass %. Changes of HEC molecular mass distribution after nitro group reduction and after the corresponding azide synthesis were, owing to fair solubility of these products, followed by means of water solution fractionation on hydrophilic gel Sephadex G-15.

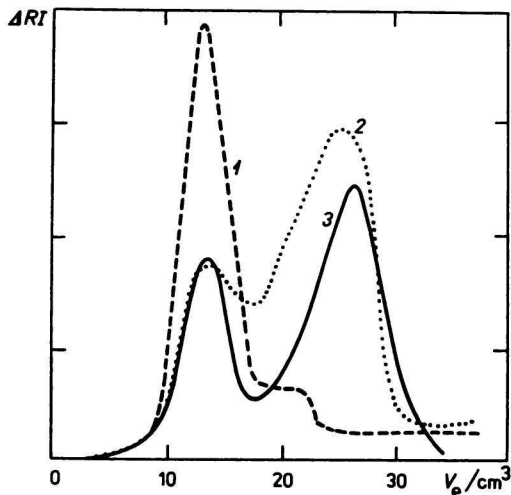


Fig. 1. GPC elution curves of the original hydroxyethylcellulose (1), the aromatic HEC nitro derivative (2), and of product II (3).

As shown by GPC analysis (Fig. 1, curve 2), during nitro group reduction the high-molecular polymer portion further decreased and the elution curve exhibits an expressive bimodal character. The high-molecular portion of the amino derivative represents only 20 mass % of the original polymer. After azide syn-

thesis an important degradation of the high-molecular polymer portion was not observed (Fig. 1, curve 3). After separation of the low-molecular from high-molecular fractions by repetitive Sephadex fractionation, elemental analysis showed that the nitrogen content in both fractions differed only slightly ($w_i(\text{found})$: 2.25 % N high-molecular and 2.56 % N low-molecular portion), which shows that distribution changes of polymer mass during synthesis do not influence the reaction process and the representation of aryl chromophores.

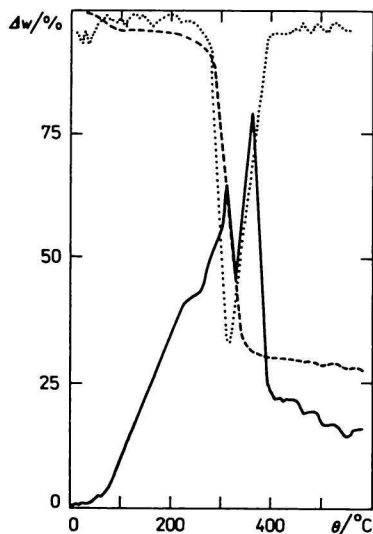


Fig. 2. Curves of thermogravimetric analysis (---), differential thermal gravimetry (.....), and differential thermal analysis (—) for hydroxyethylcellulose.

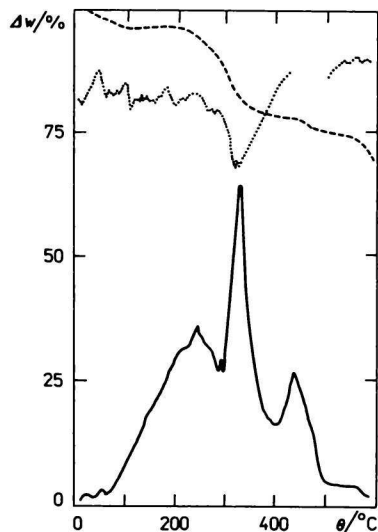


Fig. 3. Curves of thermogravimetric analysis (---), differential thermal gravimetry (.....), and differential thermal analysis (—) for product II.

UV and IR spectra of synthesized cellulose derivatives are shown in Table 1. Azido derivatives show in UV area absorption maxima $\lambda_{\text{max}} = 273$ nm for product I and $\lambda_{\text{max}} = 268$ nm for product II.

Our results correspond well with spectra of low-molecular aromatic azides [1]. In IR spectra we measured strong absorption bands of N_3 group; absorption band of stretching vibration $\tilde{\nu}_{\text{as}}(\text{N}_3) = 2124 \text{ cm}^{-1}$ for product I and $\tilde{\nu}_{\text{as}}(\text{N}_3) = 2100 \text{ cm}^{-1}$ for product II, and an absorption band of bending vibrations $\sigma(\text{N}_3) = 680 \text{ cm}^{-1}$ for both products. In both derivatives identical positions of absorption bands for nitro group stretching vibration were observed $\tilde{\nu}_{\text{as}}(\text{NO}_2) = 1520 \text{ cm}^{-1}$ and $\tilde{\nu}_s(\text{NO}_2) = 1345 \text{ cm}^{-1}$.

Application of aromatic azides is substantially influenced by the thermal characteristic of the compound. Fig. 2 shows curves of thermal gravimetry (TG) and of differential thermal analysis (DTA) for HEC used for synthesis of product *II*. The TG curve demonstrates that substantial HEC mass losses occur approximately between 270—330 °C. With product *II* (Fig. 3) this occurs in the range 230—330 °C. As far as the mass loss of HEC is as much as 76 %, with azidoaryl derivatives it is only 22 mass %, whereby even at 500 °C it increases only to 25 mass % of mass loss. This anomaly of aromatic azide thermal stability may be explained by crosslinkage reaction probably connected with thermal decomposition of azido group and the arising of free radicals. Course of DTA curves confirms occurrence of exothermal decomposition processes.

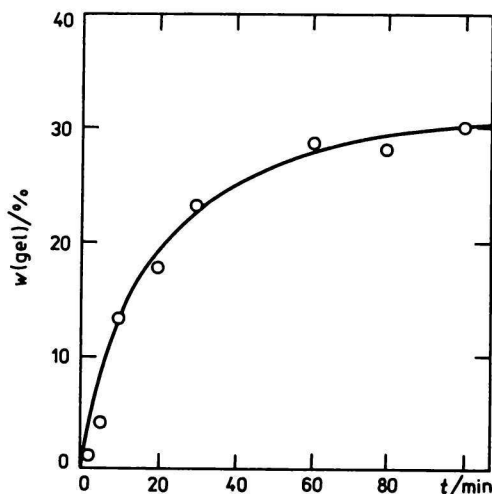


Fig. 4. Dependence of the gel portion as irradiation time function for HEC polymeric film and product *II* composition in mass ratio 1:1.

Decomposition of azido group is important for photochemical reactions. The photochemical activity was followed in both synthesized derivatives in ethanol solution. In both cases a decrease in absorption bands was observed until the azido group decomposed completely. Product *II* was finally submitted to photolysis in solid phase. Fig. 4 shows the dependence of gel portion on exposition time for polymeric film representing composition of HEC and product *II*.

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