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SYNTHESIS AND RADICAL POLYMERIZATION OF BENZAMIDMETACRYLATE

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Abstract: *The data on the synthesis of the new monomer benzamidmetacrylate are presented in the article. Its composition and structure were established by physical and chemical methods of research. The regularities of radical homopolymerization reactions in mass and in benzene solution were studied with the aim of creating a new biocidal polymeric material for medical preparations.*

It is shown that polymerization under these conditions proceeds through the vinyl bond, without an induction period, at a constant initial rate without the formation of by-products, a monotonic increase in conversion up to 92% with the formation of a soluble polymer is observed. The composition and structure of the obtained polymer were established by elemental and spectral analyses. It showed that the polymer was characterized by a low toxicity at a significant biocidal activity towards E.coli and St.Aureus and that this polymer can be used in various fields, in particular as a biocidal preparation, a carrier of dosage forms in medicine. In addition, this polymer also exhibites optical translucency and can be used in optics.
Keywords: *benzamide, methacrylates, polymerization, bactericidal activity*

Introduction

Recently, methacrylate polymers have been widely used to create biocidal and disinfectant agents, flocculants, as well as composite materials with bactericidal and fungicidal surface activity. Demand for biocidal preparations is particularly growing. In contrast to the data on the effect of benzamide substituents on the polymerization of vinyl monomers there are almost no data in the literature on the effect of benzamide groups on the radical polymerization rate, microstructure and other properties of the corresponding homopolymers [1-6]. The importance of synthesizing and searching for substances with biological activity still remains.

The aim of this work is to develop a method for synthesis of a new benzamidmethacrylate (BMA) monomer and study its radical polymerization in order to create a new antimicrobial material for medical preparations. By choosing benzamidmethacrylate as the object of research, it was assumed that the introduction of an amide fragment into a metacrylate monomer is likely to influence the rate of polymerization, including its greater antimicrobial properties [7-14].

Experimental part

In a flask with a reverse refrigerator, 0.5 mol of benzamide was placed in the medium of tertiary amine. Then at 30° C for 2 hours when stirring on drops added 0.6 mole of methacryloyl chloride to 30 ml of absolute benzene. Upon completion of the reaction, the mixture was extracted with sulfur ether, dried, distilled into light fractions, and then into the main fraction at a reduced pressure.

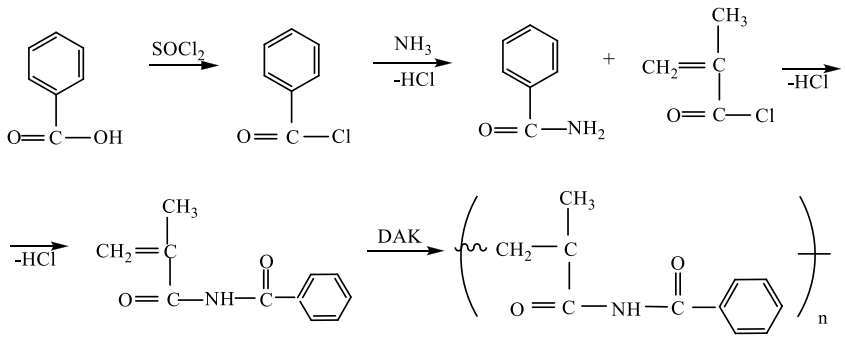
Yield (166 g.) – 95%, B. p. 110-112°C (3 mm merc.c.), n_D^{20}=1.510, d_4^{20}=1.030

Polymerization of the synthesized monomer was carried out in sealed ampoules in the atmosphere of nitrogen in a solution of benzene. The polymerization solution containing the monomer and the initiator (DAK-dinitrilazoisobutyric acid) was placed in a glass ampoule, the mixture was purged with a stream of oxygen-free nitrogen for 8 minutes, and then the tube was tightly closed and placed in a thermostat at 343 K. The amount of initiator was 0.3% of total mass

of the monomer. The resulting polymer was purified by double reprecipitation from benzene solution in methanol and dried at reduced pressure (15-20 mm merc.c.) at 30 °C to constant mass. The characteristic viscosity was established in benzene in an Ubbelode viscometer. The characteristic viscosity was ([η]=0.82 dl/g). The determination of light transmission was carried out using a photocolorimeter-nephelometer type FEK-N-57.

The IR spectra of the polymer were recorded on an ALPHA IR Fourier instrument (Bruker, Germany), the spectra of ^{1}H NMR were obtained on a Bruker AFR-300 spectrometer in $CDCl_3$, the chemical shifts were established relative to tetramethylsilane. The purity of the synthesized monomer was controlled by gas-liquid chromatography (GLC) and was 98.5%. Elemental analysis of $C_{11}O_2H_{11}N$, calculated %, C=73.3 ; H=6.11; N=7.77; found % C=73.1; H=6.11; N=7.76

Monomer synthesis and radical polymerization were carried out using of the following reaction.



The polymerization was carried out in a benzene solution, as well as in a mass in the presence of azoisobutyric acid dinitrile (AAD). The concentration of monomer and initiator was 1 mol/l and 0.3 % respectively.

The polymerization process proceeds under the studied conditions without an induction period with a constant initial rate smoothly, without the formation of byproducts, monotonically observed increase in conversion to almost 92%. The value of the characteristic viscosity of the polymer is [η]=0.82 dl/g.. It found that the acceleration of the polymerization of the monomer synthesized by us - benzamide methacrylate - in the transition from methyl methacrylate to benzamide methacrylate may be caused by the effect of the substituent on the flexibility of growing polymer chains. Based on the IR and NMR spectra of the monomer and the polymer obtained on its basis the structure of the polymer was established. The data from IR and NMR spectroscopy show that polymerization occurs on vinyl bond and are proof that benzamidetacrylate is undergoing selective vinyl polymerization by radical mechanism.

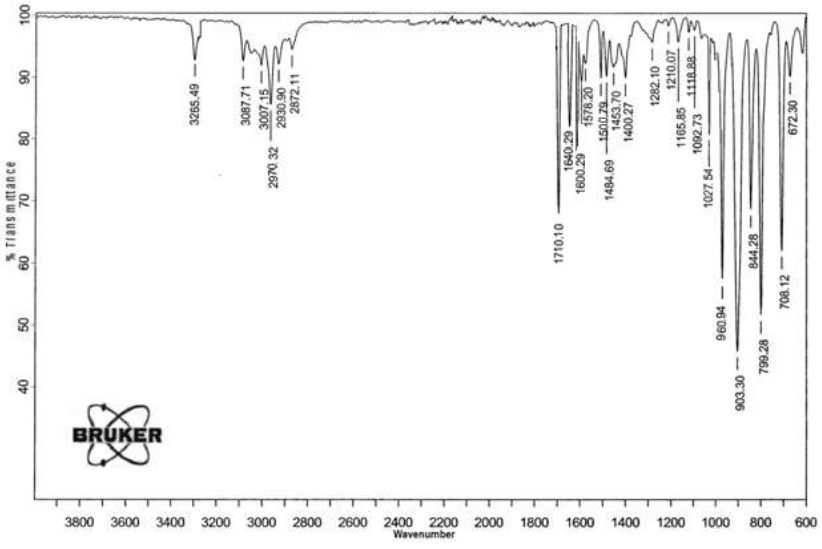


Fig. 1. IR spectra of benzamidometacrylate

In the IR spectrum of the obtained benzamidmethacrylate (BMA) monomer (Fig. 1.) and its radical polymerization, absorption bands 1710 cm^{-1} and 1640 cm^{-1} related to oscillations >C=O and >C=C< respectively, IR spectra of BMA along with the indicated absorption bands, contain bands at 960 and 2970 cm^{-1} characteristic for CH_2-C fragments and CH_3 groups, respectively [15]. In the IR spectrum of BMA has absorption bands of 1500 and 1600 cm^{-1} vibrations of the phenyl ring.

When comparing the IR spectra of the monomer and the obtained polymer based on benzamidmetacrylate, it revealed that the 1640 cm^{-1} absorption bands disappear and for the rest of the groups remain unaffected in the macrochain.

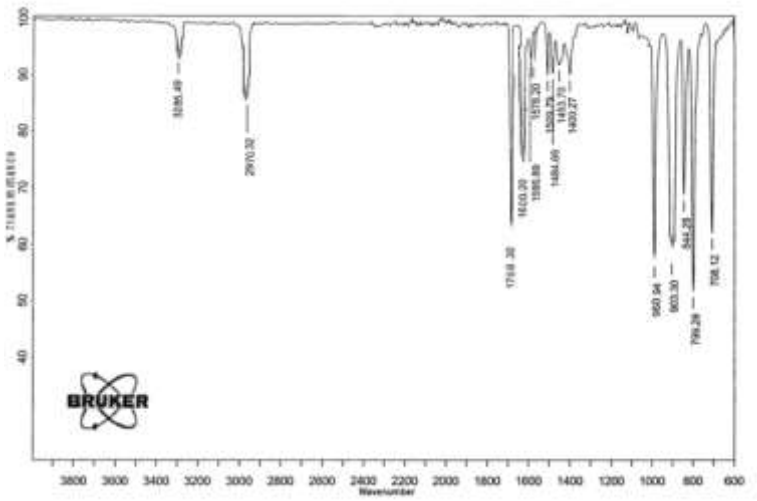
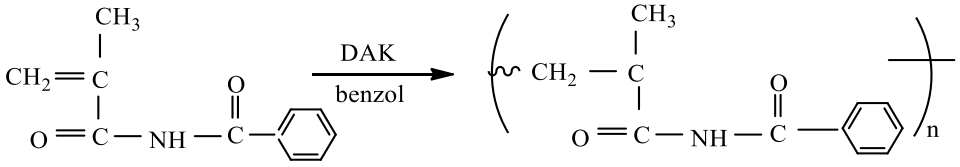


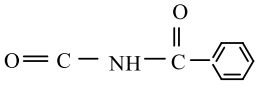
Fig. 2. IR spectra of polybenzamidometacrylate

The nature of the dependence of the polymerization rate on the depth of transformation of benzamide methacrylate and methyl methacrylate differs from most other vinyl monomers, the study of the kinetics of its polymerization indicates the presence of a self-acceleration phase, which manifests itself after the reaction to depth of 20-25% and is explained by the decrease in the rate constant of chain termination due to an increase in the viscosity of the medium [16].

The polymer was precipitated twice in methanol and dried in vacuo, the molecular weight estimated by gel permeation chromatography was 55000. The IR and NMR spectroscopy data indicate the polymerization on the vinyl bond and are evidence of the polymerization of this benzamide methacrylate by a radical mechanism. As a result, benzamide fragments remain unaffected in the side macrochain.



In order to disclose the effect of the benzamide substituent in the methacrylate monomer, the polymerization of methyl methacrylate was studied under similar conditions. The results are presented in Fig. 3.

The Fig.3 shows that the polymerization of benzamidmethacrylate proceeds at a high rate above the polymerization rate of methyl methacrylate, but is nearly over at 92% conversion. In the presence of group  as a result of conjugation and polarization of the vinyl group, the reactivity of the monomer increases.

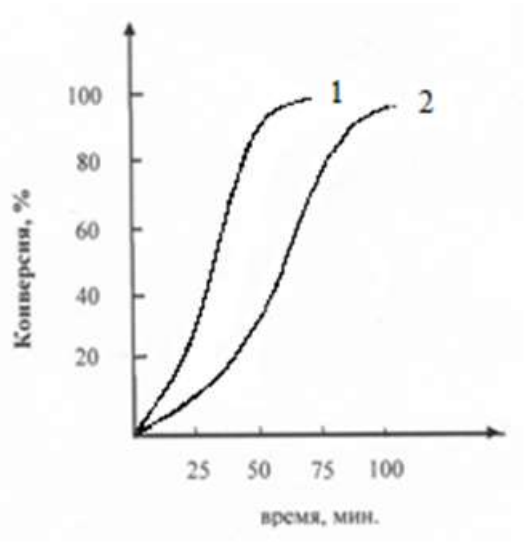


Fig. 3. Kinetic curves of benzamidometacrylate (1) and metylmetacrylate (2)

UV spectra (Fig. 4) of benzamidmethacrylate and methyl methacrylate are removed under same conditions. As can be seen from the Fig.4, the maximum absorption of benzamidmethacrylate in the UV spectra compared to the MMA is shifted towards long waves (280 nm). This is due to the fact that the conjugation effect of the substitutes is known to cause greater shifts in the absorption spectra than the inductive effect.

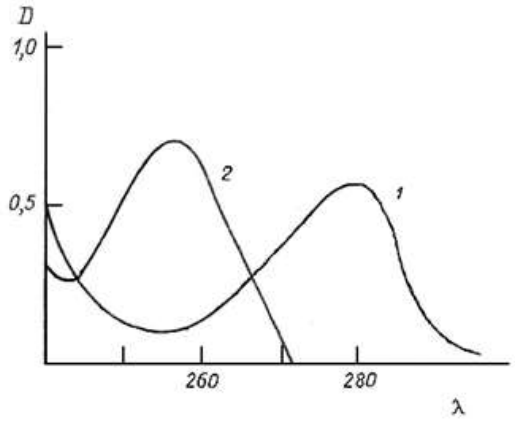


Fig. 4. UV spectra of benzamidometacrylate (1) and metylmetacrylate (2)

The synthesized polymer also has bactericidal activity which is due to the presence of benzoamide fragment links in the side chain. The polymer exhibits the highest bactericidal and fungicidal activity against some microorganisms at the following concentrations (wt%):E.coli – 1.8; St.aureus – 0.9; Can.alb. – 0.9.

It was shown that with significant biocidal activity against E. coli and St. aureus the synthesized polymer is characterized by low toxicity.

Based on these studies it can be concluded that the strategy for the creation of polymers with high biocidal activity should include polymerization with other methacrylate monomers.

In addition, the synthesized polymer also possesses good optical indices n_D^{20}=1.510. It was found that the obtained polymer retained its translucency up to 100°C when exposed for 1.2 hours. It was shown that the transmittance in the visible part of the spectrum is 90-92% and depends little on the sample thickness up to 6-8 mm.

Thus, this work describes the synthesis of a representative of a new monomer and a polymer derived from it and proves their structure. This polymer can be used in various applications such as biocidal agent, dosage form carrier in medicine, it is also optically transparent material and can be used in optics.

References

1. Misin V.M., Zezin A.A., Klimov D.I., Sybachin A.V., Yaroslavov A.A. Biocidal Polymer Formulations & Coatings. *Polymer Science, Series B.* 2021, vol. 63, no 5, pp. 295-306 (In Russian) **DOI:** 10.1134/s1560090421050079
2. Ivashev M.N., Kruglaya A.A., Savenko I.A. Usmansky Yu.V., Sergienko A.V., Lysenko T.A., Kuyantseva A.M., Arlt A.V., Zatsepina E.E., Efremova M.P., Shemonaeva M.V., Maslikova G .V., Sampieva K.T., Strugovshchik Yu.S., Vrubel M.E., Alieva M.U. Biological activity of compounds obtained synthetically. *Fundamental'nyye issledovaniya*. 2012, no.7, pp. 441-444 (In Russian).
3. Plate N.A., Ponomarenko A.G. Kinetic features of radical polymerization of n-alkyl methacrylates. *Polymer Science.* 1974, vol.XVI, no. 12, pp. 2635-2645 (In Russian).
4. Shtilman M.I., Tsatsakis A.M., Vlahos J.C., Dragassaki M., Shashkova I.M., Hydrolysis and biological activity in a series of water-soluble polymeric esters of aryl-containing carboxylic acids. *Polymer Science,* Series A, 1997, vol. 39, no 11, pp.1761-1766 (In Russian).
5. Sivova N.A., Menyasheva M.R., Gerasina V.A., and Kleshcheva N.A. Copolymerization of methacryloylguanidine trifluoroacetate with styrene in acetone and dimethyl sulfxide at high degrees of conversion. *Polymer Science,* Series B, 2019, vol. 61, no 1, pp. 30–34 (In Russian).
6. Sivov N.A., Kleshcheva N.A., Valuev I.L., Valuev L.I. Biocidal copolymers of methacryloylguanidine hydrochloride with methacrylamide and diallyldimethylammonium chlorides. *Polymer Science,* Series B, 2021, vol. 63, no 5, pp. 340–344 (In Russian).
7. O.B.Abdiyev, E.G.Mamedbeyli, Polymerization of aryl derivative unsaturated carbonyl compounds and their copolymerization with methyl-2- chloracrylate, glycidyl-methacrylate, methacrylic acid and l-(-)-menthylmethacrylates. *Chemical problems*. 2013, no. 1, pp. 34-44.
8. Panarin E.F., Biologically active polymer nanosystems. *Russian Chemical Bulletin*. 2017, no 10. pp. 1812-1820 (In Russian).
9. Lavrov N.A., Shal´nova L.I., Specific features of preparation of polymer-carriers of physiologically active substances based on N-vinylsuccinimide derivates. *Polymer Science.* Ser.D. 2012, vol.5, no.3, pp. 202-20. (In Russian).
10. Tatsuo Tashiroa, Antibacterial and Bacterium Adsorbing Macromolecules. *Macromol. Mater*. Eng. 2001, vol. 286, pp. 63–87.
11. El-Refaie Kenawy, S. D. Worley, and Roy Broughton, The Chemistry and Applications of Antimicrobial Polymers: A State-of-the-Art Review. *Biomacromolecules.* 2007, vol. 8, no. 5, pp. 1359-1384.
12. Munoz-Banilla A., Fernandez-Garcia M. Polimeric materials with antimicrobial activity. *Progress Polymerr. Sci*. 2012, vol. 37, pp. 281-339.
13. Dontsova E.P., Zharnenkova O.A., Snezhko A.G., Uzdensky V.B. Polymeric materials with antimicrobial properties. *Plastic.* 2014, vol. 131, no. 1-2, pp. 30-35 (In Russian).
14. Kenawy E.-R., Abdel-Hay F. I., A. E.-R. R. El-Shanshoury, and M. H. El-Newehy, Biologically active polymers: synthesis and antimicrobial activity of modified glycidyl methacrylate polymers having a quaternary ammonium and phosphonium groups. *Journal of Controlled Release*. 1998, vol. 50, no. 1–3, pp. 145–152.
15. Simon W, Clerc T. Structural Analysis of org. Compas. By spectroscop. Methods. 1971, *Makdonald and Co.,* pp. 47-58.
16. Lachinov M.B., Korolev B.A., Dreval V.E., Cheren E.I., Zubov V.P., Kobanov V.A. Relation of autoacceleration in radical polymerization. *Polymer Science* 1982, vol. 24A, no. 10, pp. 2220-2226.

BENZAMİDMETAKRİLATIN SİNTEZİ VƏ RADİKAL POLİMERLƏŞMƏSİ

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Xülasə: Məqalə üzrə təqdim olunan məlumatlarda yeni benzamidmetakrilat monomerinin sintezi verilmişdir. Onun tərkibi və quruluşu fiziki-kimyəvi tədqiqat üsulları ilə müəyyən edilmişdir. Tibbi preparatlar üçün yeni biosidal polimer material yaratmaq məqsədi ilə kütlədə və benzol məhlulunda radikal homopolimerləşmə reaksiyalarının qanunauyğunluqları öyrənilmişdir. Göstərilmişdir ki, bu şəraitdə polimerləşmə yan makrozəncirdə saxlanılan əvəzedici ilə vinil qrupunda gedir. Müəyyən edilmişdir ki, polimerləşmə prosesi induksiya dövrü olmadan, mütəmadi olaraq ilkin sürətlə, heç bir yan məhsul əmələ gəlmədən, 92%-ə qədər çevrilmələrin artması ilə həll ola bilən polimerin əmələ gəlməsi ilə müşayiət olunur. Alınmış polimerin element və spektral analizlər üzrə tərkibi və quruluşu müəyyən edilmişdir. Sintez edilmiş yeni benzamid polimerinin bakterisid və toksikoloji sınaqları aparılmışdır. Müəyyən olunmuşdur ki, polimerin E. coli və St. Aureusa qarşı əhəmiyyətli biosid aktivliyi və aşağı toksikliyi ilə xarakterizə olunur. Göstərilmişdir ki, bu polimer müxtəlif sahələrdə, xüsusən də tibdə biosidal preparat və dozaj formalarının daşıyıcısı kimi istifadə edilə bilər. Bundan əlavə, bu polimer həm də optik şəffaflıq nümayiş etdirir və optikada istifadə edilə bilər.
Açar sözlər: benzamid, metakrilatlar, polimerləşmə, bakterisid aktivlik

СИНТЕЗ И РАДИКАЛЬНАЯ ПОЛИМЕРИЗАЦИЯ БЕНЗАМИДМЕТАКРИЛАТА

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Аннотация: В представленной статье приведены данные по синтезу нового мономера бензамидметакрилата. Физико-химическими методами исследования устоновлены его состав и структура. Изучены закономерности реакции радикальной гомополимеризации в массе и в растворе бензоле с целью создания нового биоцидного полимерного материала для медицинских препаратов. Показано, что полимеризация в указанных условиях протекает по виниловой связи, без индукционного периода с постоянной начальной скоростью без образования побочных продуктов, наблюдается монотонное увеличение конверсии до 92% с образованием растворимого полимера. Установлены состав и структура полученного полимера по данным элементного и спектральных анализов. Проведены бактерицидные и токсикологические испытания синтезированного нового бензамидного полимера на ряде клеточных культур. Показано, что при значительной биоцидной активности полимера по отношению к E.coli и St.Aureus он характеризуется невысокой токсичностью и может использоваться в различных областях, в частности, как биоцидный препарат, носитель лекарственных форм в медицине. Кроме того, полимер проявляет оптическую прозрачность и может быть использован в оптике.
Ключевые слова: бензамид, метакрилаты, полимеризация, бактерицидная активность.