# STUDY OF THE RADICAL POLYMERIZATION PROCESS OF 6-BROMO-BOMMA

**Mustafoev Khusen Mamedkulovich**
*Associate Professor of Bukhara State Pedagogical Institute*
*E-mail: mustafoyev_husen@buxdpi.uz*
**Sharipov Ilkhom Khusenovich**
*Associate Professor of Bukhara State Pedagogical Institute*
**Naimova Roziya Nodir qizi**
*Master's student at Bukhara State Pedagogical Institute*

**Abstract.** This article examines the photo- and thermal stabilization of homo- and copolymers of methyl methacrylate and acrylamide containing stabilizing groups. The thermal and thermo-oxidative degradation of polymers and copolymers of 6-bromobenzoxazolonyl methyl methacrylate, along with changes in their molecular weight during decomposition, were analyzed using thermogravimetric analysis, chromatography, and manometry. The study found that incorporating small amounts (0.5–3.0 mass%) of 6-Br-BOMMA units into the main chain of polyacrylamide (PAA) and polymethyl methacrylate (PMMA) significantly slows thermal degradation. Additionally, the most pronounced stabilization against photodegradation occurs at 0.5–1.0 mass% of 6-Br-BOMMA, highlighting the high efficiency of intramolecular stabilization.

**Keywords:** Polymer stabilization, Photo-stabilization, Thermal stabilization, Radical polymerization, Thermo-oxidative degradation, Methyl methacrylate, Acrylamide, Polymethyl methacrylate, Polyacrylamide, 6-Bromo-benzoxazolonyl methyl methacrylate, Copolymerization.

**Аннотация.** В данной статье рассматривается фото- и термическая стабилизация гомо- и сополимеров метилметакрилата и акриламида, содержащих стабилизирующие группы. Термическое и термоокислительное разложение полимеров и сополимеров 6-бромбензоксазолонилметилметакрилата, а также изменения их молекулярной массы в процессе деструкции были проанализированы с использованием термогравиметрического анализа, хроматографии и манометрии. Установлено, что введение небольших количеств (0,5–3,0 мас.%) звеньев 6-Br-BOMMA в основную цепь полиакриламида (PAA) и полиметилметакрилата (PMMA) значительно замедляет их термическое разложение. Кроме того, наибольший стабилизирующий эффект по отношению к фотодеструкции наблюдается при содержании 0,5–1,0 мас.% 6-Br-BOMMA, что свидетельствует о высокой эффективности внутримолекулярной стабилизации.



ISSN 3030-3907

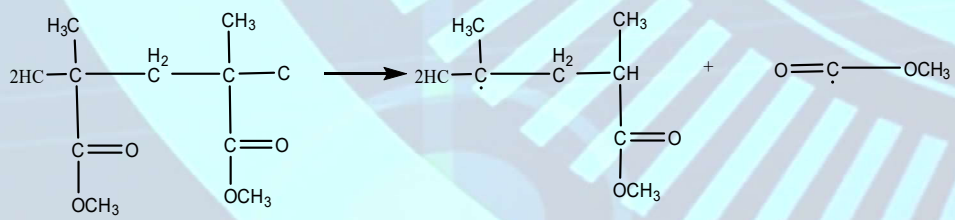
**Ключевые слова:** стабилизация полимеров, фотостабилизация, термическая стабилизация, радикальная полимеризация, термоокислительное разложение, метилметакрилат, акриламид, полиметилметакрилат, полиакриламид, 6-бромбензоксазолонилметилметакрилат, сополимеризация.

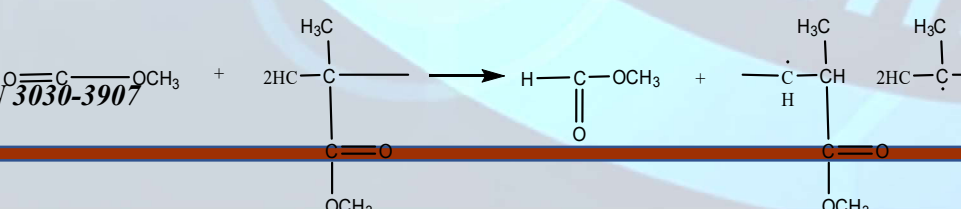
**Annotatsiya.** Ushbu maqolada stabilizatsiyalovchi guruhlarga ega metil metakrilat va akrilamidning gomo- va sopolimerlarining foto- va termik barqarorligi o‘rganilgan. 6-brombenzoksazolonil metil metakrilat asosidagi polimerlar va sopolimerlarning termik va termo-oksidlovchi yemirilishi, shuningdek, yemirilish jarayonida ularning molekulyar massasi o‘zgarishi termogravimetrik tahlil, xromatografiya va manometriya usullari yordamida tahlil qilindi. Tadqiqot natijalariga ko‘ra, poliakrilamid (PAA) va polimetilmetakrilat (PMMA) asosiy zanjiriga 6-Br-BOMMA birikmasining kichik miqdorlari (0,5–3,0 massa%) qo‘shilishi ularning termik yemirilishini sezilarli darajada sekinlashtiradi. Bundan tashqari, fotoyemirilishga nisbatan eng yuqori barqarorlashtiruvchi ta’sir 0,5–1,0 massa% 6-Br-BOMMA miqdorida kuzatiladi, bu esa intramolekulyar stabilizatsiyaning yuqori samaradorligini ko‘rsatadi.

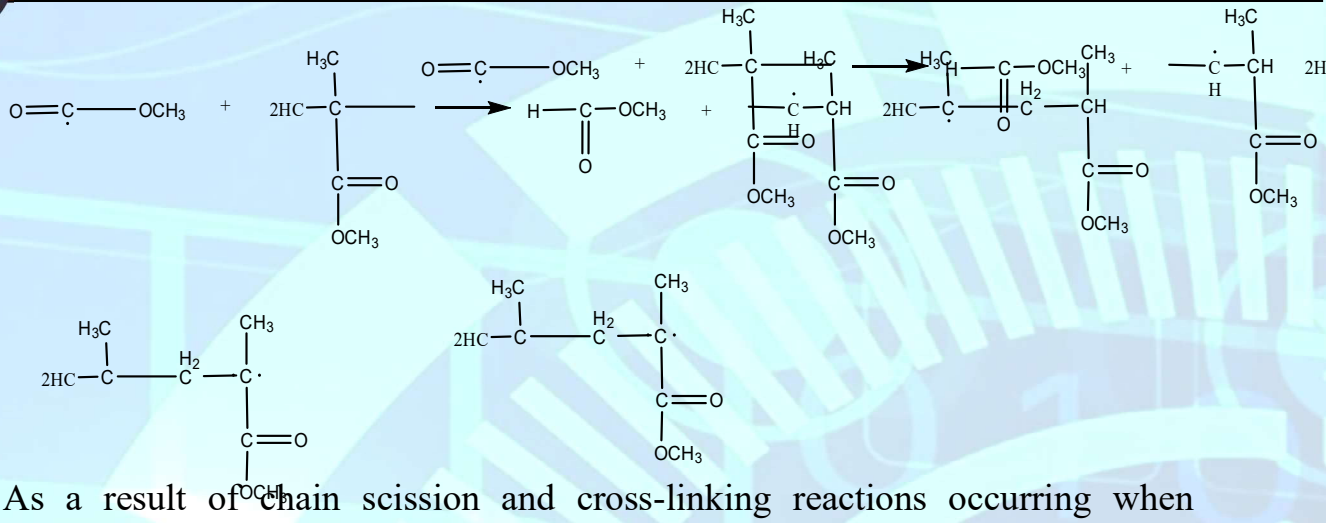
**Kalit so‘zlar:** polimerlarni stabilizatsiyalash, foto-stabilizatsiya, termik stabilizatsiya, radikal polimerlanish, termo-oksidlovchi yemirilish, metil metakrilat, akrilamid, polimetilmetakrilat, poliakrilamid, 6-brombenzoksazolonil metil metakrilat, sopolimerlanish.

## Introduction

Photodestruction can be slowed down by introducing special photostabilizers or UV absorbents that can inhibit the process and significantly increase the service life of polymer products. An interesting example of photodestruction is the depolymerization of PMMA, which occurs in the melt under the action of UV irradiation with a quantitative yield of monomer. At the beginning of photodestruction [1], free radicals are formed and the further course of the process with their participation significantly depends on the physical state of the polymer material [2, 3]. Thus, PMMA in the melt degrades to a monomer, but in the solid state under the same conditions, almost no monomer is formed. However, in the process of photodestruction of solid PMMA, a small amount of methyl formate is formed according to the following scheme [4, 5]:









As a result of chain scission and cross-linking reactions occurring when polymers are irradiated with UV light, the molecular weight changes significantly. Therefore, determining the molecular weight is a task of paramount importance when identifying the mechanisms of photoreactions in polymer systems [6].

**MATERIALS AND METHODS**

The synthesized homo- and copolymers are characterized by the presence of chromophore groups capable of absorbing UV light in the region of 200-350 km. In this regard, it is of particular interest to study the influence of these groups on the photostability of polymers.

Based on the above, the results of studies of photodestruction of polymers and copolymers based on polyacrylamide (PAA) and polymethyl methacrylate (PMMA) using UV irradiation are presented. It was found that irradiation of PAA and PMMA with UV light in air leads to strong yellowing, as well as to a decrease in physicochemical properties and eventually to destruction [7–10]. The quantum yield of the discontinuity was estimated using the following equation:

$$\varphi = \frac{S * N}{M_n * I_\rho},$$

where $N$ is the number of scissions in one medium of a numerical macromolecule; K- is Avogadro's constant; $M_n$ is the number average molecular weight of the original polymer: $I_\rho$ is the number of absorbed light quanta.

The number of chain scissions was determined by the following formula:

$$S = \left[\frac{[\eta_0]}{[\eta]}\right]^{1/\alpha} - 1,$$

where $[\eta_0]$, $[\eta]$ are the characteristic viscosities of the polymer before and after irradiation.

$\alpha$ is the exponent in the Mark-Hauvink, equal to 0.80 for PAA in water and 0.77-1761 for PMMA in benzene.



ISSN 3030-3907

With the above formula, it is possible to calculate the irradiation of optically "thin" films; to consider changes in the molecular weight distribution of the polymer, it is necessary to introduce special additives. When irradiating optically "dense" solutions, this limitation is removed by sufficiently effective mixing of the solution. The value of the stability coefficient was calculated.

$$K = \frac{[\eta]}{[\eta_0]}.$$

**Results**

It was revealed that an increase in temperature contributed to an increase in photodestruction, i.e. a decrease in intrinsic viscosity values leading to a decrease in the molecular weight of macromolecules (Tables 1-2).

**Table 1.**

**Dependence of intrinsic viscosity of copolymers on the irradiation time at T=298K. (PAA, PMMA are takenas films, distance from the source is 30 cm)**

| N | System | Time, hour | Reduced viscosity | | Number of scissions in the chain | Stability coefficient Rst, % |
|---|---|---|---|---|---|---|
| | | | Original $\eta_0$ | After photodestruction, $\eta$ | | |
| 1 | PAA | 3 | 1.78 | 0.34 | 6.91 | 19.10 |
| | | 9 | | 0.20 | 14.3 | 11.23 |
| | | 18 | | 0.17 | 17.8 | 9.55 |
| | | 30 | | 0.13 | 25.3 | 7.3 |
| 2 | PMMA | 3 | 1.84 | 0.42 | 5.72 | 22.82 |
| | | 9 | | 0.26 | 10.32 | 15.21 |
| | | 18 | | 0.24 | 12.8 | 13.04 |
| | | 30 | | 0.226 | 13.9 | 12.28 |
| 3 | PAA+0,5% 6-Br-BOMMA | 3 | 1.72 | 0.63 | 2.5 | 36.62 |
| | | 9 | | 0.49 | 3.8 | 28.48 |
| | | 18 | | 0.433 | 4.6 | 25.17 |
| | | 30 | | 0.354 | 6.21 | 20.58 |
| 4 | PMMA+0,5% 6-Br-BOMMA | 3 | 1.81 | 0.67 | 2.6 | 37.01 |
| | | 9 | | 0.50 | 3.54 | 30.93 |
| | | 18 | | 0.47 | 4.69 | 25.96 |
| | | 30 | | 0.41 | 5.79 | 22.65 |
| 5 | PAA+1% 6-Br-BOMMA | 3 | 1.69 | 0.73 | 1.85 | 43.19 |
| | | 9 | | 0.67 | 2.17 | 39.64 |
| | | 18 | | 0.45 | 4.22 | 26.62 |



ISSN 3030-3907

| | | | | | | |
|---|---|---|---|---|---|---|
| | | 30 | | 0.43 | 4.47 | 25.68 |
| 6 | PMMA+1 % 6-Br-BOMMA | 3<br>9<br>18<br>30 | 1.78 | 0.79<br>0.76<br>0.52<br>0.509 | 1.84<br>1.99<br>3.89<br>4.02 | 44.38<br>42.69<br>29.21<br>28.59 |
| 7 | PAA+3% 6-Br-BOMMA | 3<br>9<br>18<br>30 | 1.76 | 0.52<br>0.38<br>0.33<br>0.29 | 2.59<br>5.79<br>7.1<br>8.52 | 29.54<br>21.59<br>18.75<br>16.47 |
| 8 | PMMA+3 % 6-Br-BOMMA | 3<br>9<br>18<br>30 | 1.82 | 0.57<br>0.44<br>0.41<br>0.37 | 3.47<br>5.24<br>5.83<br>6.8 | 31.31<br>24.17<br>22.52<br>20.32 |

Note: UV irradiation source is lamp, DRT-1000, λ=200-350 nm UV-1 light filter.

**Table 2.**

**Dependence of intrinsic viscosity of copolymers on the irradiation time at T=323K (PAA, PMMA are taken as films, distance from the source is 30 cm)**

| N | System | Time, hour | Reduced viscosity | | Number of scissions in the chain | Stability coefficient Rst, % |
|---|---|---|---|---|---|---|
| | | | Original $\eta_0$ | After photodestruction $\eta$ | | |
| 1 | PAA | 3<br>9<br>18<br>30 | 1.53 | 0.46<br>0.33<br>0.31<br>0.28 | 4.42<br>7.22<br>788<br>9.15 | 25.84<br>18.53<br>17.41<br>15.73 |
| 2 | PMMA | 3<br>9<br>18<br>30 | 1.59 | 0.54<br>0.41<br>0.38<br>0.354 | 3.86<br>5.93<br>6.65<br>7.38 | 29.34<br>22.28<br>20.65<br>19.23 |
| 3 | PAA+0.5% 6-Br-BOMMA | 3<br>9<br>18<br>30 | 1.47 | 0.773<br>0.612<br>0.54<br>0.497 | 1.71<br>2.63<br>3.25<br>3.72 | 44.94<br>35.58<br>31.39<br>28.89 |
| 4 | PMMA+0.5% | 3<br>9<br>18 | 1.56 | 0.82<br>0.68<br>0.59 | 1.77<br>2.53<br>3.24 | 45.30<br>37.56<br>32.59 |



ISSN 3030-3907

| | | | | | | |
|---|---|---|---|---|---|---|
| | 6-Br-BOMMA | 30 | | 0.56 | 3.54 | 30.93 |
| 5 | PAA+1% 6-Br-BOMMA | 3<br>9<br>18<br>30 | 1.42 | 0.862<br>0.763<br>0.582<br>0.562 | 1.32<br>1.7<br>2.75 | 51<br>45.14<br>34.43<br>33.25 |
| 6 | PMMA+1 % 6-Br-BOMMA | 3<br>9<br>18<br>30 | 1.51 | 0.91<br>0.87<br>0.64<br>0.63 | 1.37<br>1.51<br>2.74<br>2.81 | 51.12<br>48.87<br>35.95<br>35.39 |
| 7 | PAA+3% 6-Br-BOMMA | 3<br>9<br>18<br>30 | 1.44 | 0.632<br>0.491<br>0.457<br>0.429 | 2.59<br>3.93<br>4.39<br>4.83 | 35.90<br>27.89<br>25.96<br>24.37 |
| 8 | PMMA+3 % 6-Br-BOMMA | 3<br>9<br>18<br>30 | 1.49 | 0.71<br>0.58<br>0.53<br>0.516 | 2.36<br>3.37<br>3.91<br>4.08 | 39.01<br>31.86<br>29.12<br>28.35 |

Note. UV irradiation source is lamp DRT-1000, A-200-350 m. UV filter UV-1.

Based on experimental data, it was established that the introduction of small amounts of 6-Br-BOMMA into the macromolecular chains of PAA and PMMA significantly changes the photostability of the polymer.

An increase in temperature contributed to an increase in photodestruction, which led to a decrease in molecular weight and an increase in the intrinsic viscosity of macromolecules. It was revealed that the synthesized polymer stabilizer is an effective photostabilizer.

The continuous growth in production and a wide range of applications of homo- and copolymers based on acrylamide and methyl methacrylate in various industries necessitates a detailed study of their behavior at high temperatures, radiation, and other factors, the influence of which creates conditions for the occurrence of chemical transformations (cyclization) in polymers, copolymers leading to the loss of a complex of valuable physical and chemical properties and a reduction in the service life of polymers and products based on them. Thus, the study of the kinetics and mechanism of thermal, thermo-oxidative destruction of polymers is of certain theoretical and practical significance.

The results of studies of the thermal and thermo-oxidative destruction of polymers and copolymers of acrylamide, methyl methacrylate using



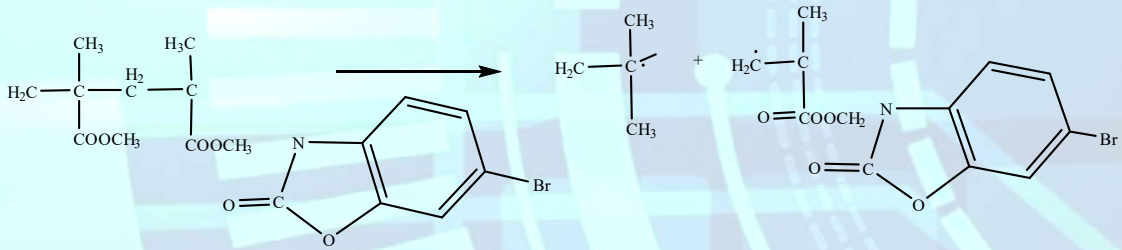
ISSN 3030-3907

thermogravimetric analysis, chromatography, monometry, and changes in the molecular weight of homo- and copolymers during their destruction were obtained.

The results of dynamic thermogravimetry of acrylamide and methyl methacrylate polymers, as well as copolymers with minor (0.5-3.0 wt.%) amounts of 6-bromo-BOMA, show, that samples modified with 6-bromo-BOMA units have higher thermal stability than PAA and PMMA. In this case, the onset of thermo-oxidative decomposition shifts to the region of higher temperatures. The stabilizing properties of monomer stabilizers are most effectively manifested when the copolymer structure contains 0.5-1.0 wt% of 6-bromo-BOMMA units (Table 3).

The thermal-oxidative decomposition of polymers and copolymers is autocatalytic. This means that the mass of the studied samples decreases slowly at the beginning of destruction, and then the loss of mass occurs more quickly in a relatively narrow temperature range. The autocatalytic pattern of the decomposition process is due to the accumulation of structures with terminal not-saturated groups, the strength of which at high temperatures decreases due to the difference in the vibrational resonance of the bond.

In addition, this is apparently due to the decomposition of the resulting peroxide groups in the copolymer structure, the stability of which at high temperatures is measured in fractions of a second. As a result, disproportionation reactions can occur by the following scheme:



Using the Reich method, the activation energy for the decomposition process of polymers and copolymers of acrylamide and methyl methacrylate with 6-Br-BOMMA was determined (Table 3). It can be seen that the introduction of small amounts of stabilizer monomer units into the structure of the main polymer leads to an increase in the apparent energy of thermal oxidative decomposition by 50-55 kJ/mol of unstabilized PAA samples and activation relative to PMMA. To establish the mechanism of thermal-oxidative degradation and determine effective amounts of stabilizers, it was necessary to determine the composition of gaseous and liquid products of destruction and study degraded polymer samples.

It was determined that ammonia and water are released as volatile products during the thermal degradation of PAA at temperatures below 538 K, indicating an imide structure formation.

**Discussion**



ISSN 3030-3907

Using chromatographic studies, it was revealed that during the destruction of copolymers 6-Br-BOMA with AA imide structures are formed. The main part of the volatile product formed is a hydroxymethyl derivative and the appearance of anhydride structures in non-volatile products suggests that during the destruction there is an interaction between neighboring amide and ester groups, accompanied by the release of hydroxymethylol 6-Br-BOMA:

**Table 3**

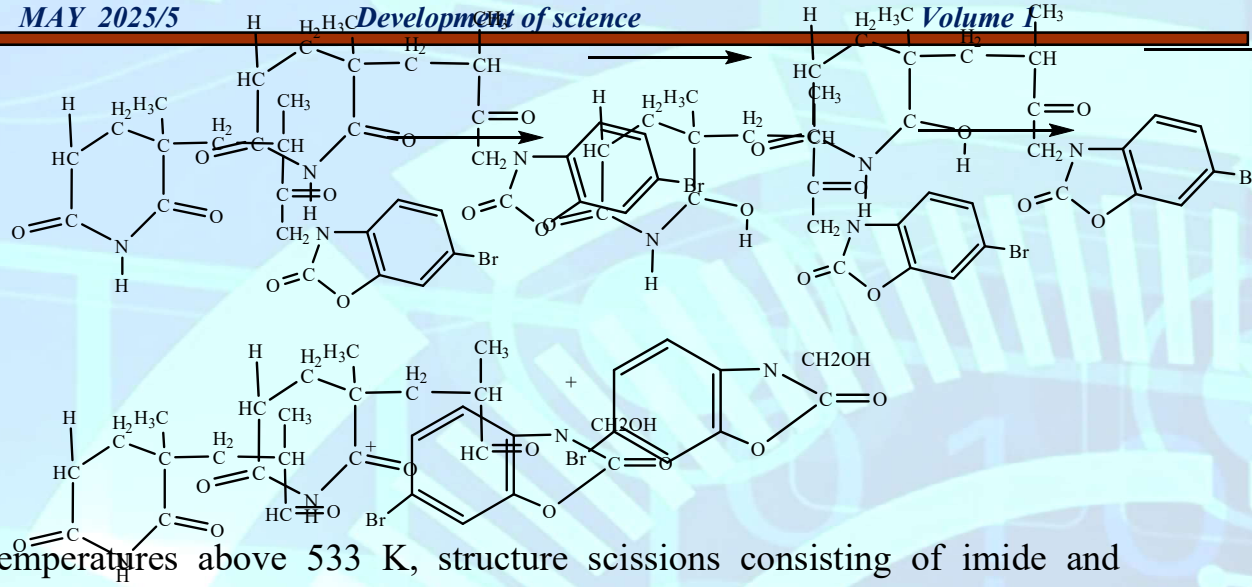
**Parameters of thermo-oxidative degradation of chemically stabilized samples of polyacrylamide and polymethyl methacrylate at non-isothermal oxidation in air at a heating rate of 10o/min. Dependence of intrinsic viscosity of copolymers on the irradiation time at T=323K (PAA, PMMA are taken as films, distance from the source is 30 cm)**

| Mass stabilizer content, % | Temperature of the onset of decomposition, K | Temperature of the maximum rate of mass loss, K | Maximum mass loss at 423 K (1) and 523K (2) | Activation energy of thermal oxidative destruction, kJ/mol |
|---|---|---|---|---|
| **6-Br-BOMA-AA (1)** | | | | |
| 0 | 380 | 475 | 95 | 123.0 ± 1.5 |
| 0,5 | 460 | 538 | 46 | 178.3 ± 1.2 |
| 1,0 | 448 | 523 | 54 | 163.4 ± 1.8 |
| 2,0 | 433 | 504 | 63 | 145.6 ± 1.3 |
| 3,0 | 425 | 485 | 78 | 138.2 ± 2.1 |
| **6-Br-BOMA-MMA (2)** | | | | |
| 0 | 433 | 613 | 93 | 150.0 ± 1.3 |
| 0,5 | 575 | 697 | 38 | 207.5 ± 1.5 |
| 1,0 | 566 | 675 | 42 | 185.3 ± 2.1 |
| 2,0 | 553 | 641 | 49 | 177.4 ± 1.8 |
| 3,0 | 542 | 627 | 63 | 163.7 ± 2.3 |

6-Br-BOMA formation of anhydride structures proceeds according to the following structure:



ISSN 3030-3907



At temperatures above 533 K, structure scissions consisting of imide and pseudoanhydride units separated by 6-Br-BOMMA and AA units occur.

**Conclusion**

Thus, the process of thermal and thermo-oxidative degradation of synthesized homo- and copolymers was studied. It was determined that the greatest effect of thermal stability in stabilized samples of PAA and PMMA copolymers is observed at a content of 0.5-1.0 wt% of 6-Br-BOMMA stabilizer units.

It was stated that the introduction of small amounts0.5-3.0 wt% of 6-Br-BOMMA units into the main chain of PAA and PMMA significantly slows down their thermal degradation; the greatest effect during photodestruction is observed at a content of 0.5-1.0 wt. % 6-Br-BOMMA units, indicating the high efficiency of intramolecular stabilization.

## REFERENCES


1. E. N. Nuraneeva, G. B. Guseva, E. V Antina, and A. I. V'yugin, "Influence of structural and solvation factors on the photodestruction and efficiency of singlet oxygen generation by luminophores based on iodo- and bromosubstituted zinc(II), cadmium(II) and boron(III) dipyrromethenates," *J. Photochem. Photobiol. A Chem.*, vol. 426, p. 113789, (2022).
2. N. M. Emanuel and A. L. Uchachenko, Chemical physics of molecular destruction and stabilization of polymers. Moscow: Nauka, 1988.
3. N. Ahmadi, G. Rezazadeh, A. Rahmani, and M. Ghanbari, "Analyzing the effects of polymeric dielectric materials on micro capacitive pressure sensors: A model incorporating displacement-dependent porosity," *Heliyon*, vol. 10, no. 9, p. e30626, (2024).
4. C. Liu, C.-Y. Zhu, C. Zhang, H.-C. Yang, and Z.-K. Xu, "Thermodynamic and kinetic understanding for managing the controllability of interfacial polymerization," *Prog. Polym. Sci.*, vol. 152, p. 101815, 2024.
5. V. R. Gowariker, N. V. Viswanathan, and D. Sridhar, *Polymers*. Moscow: Nauka, 1979.




ISSN 3030-3907

6. M. B. Boarini, N. S. Gsponer, M. E. Milanesio, and E. N. Durantini, “Porphyrin-polyethylenimine conjugates as photodynamic polymers to eliminate Staphylococcus aureus and Escherichia coli,” *Eur. Polym. J.*, vol. 200, p. 112512, (2023).
7. J. Ebdon *et al.*, “Thermal degradation and flame retardance in copolymers of methyl methacrylate with diethyl(methacryloyloxymethyl)phosphonate,” *Polym. Degrad. Stab.*, vol. 70, pp. 425–436, (2000).
8. S. Kuroda, K. Terauchi, K. Nogami, and I. Mita, “Degradation of aromatic polymers—I. Rates of crosslinking and chain scission during thermal degradation of several soluble aromatic polymers,” *Eur. Polym. J.*, vol. 25, no. 1, pp. 1–7. (1989).
9. B.-S. Kang, S. G. Kim, and J.-S. Kim, “Thermal degradation of poly(methyl methacrylate) polymers: Kinetics and recovery of monomers using a fluidized bed reactor,” *J. Anal. Appl. Pyrolysis*, vol. 81, no. 1, pp. 7–13, (2008).
10. B. A. Mavlonov, I. K. Choriev, O. M. Yariev, and G. A. Khudoynazarova, “Study of the thermal stability of chemically stabilized methyl methacrylate copolymers., Russian Federation. Patent No. 2513, (8 Septemter 2000)



ISSN 3030-3907