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FEATURES OF METHYLMETHACRYLATE THERMOPOLYMERIZATION IN THE PRESENCE OF INTRAIONIC DYES

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Abstract. The polymerization ability of methylmethacrylate (MMA) dimethylformamide (DMF) solutions in the process of their radical thermoinitiated homopolymerization in the presence of intraionic dyes was investigated by a dilatometry method. It was shown that dyes can initiate the polymerization process in the presence of standard initiator AIBN or without it. This is considerable for colored polymethylmethacrylate (PMMA) obtaining.

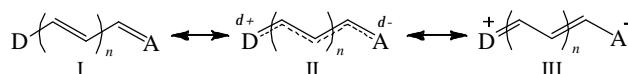
Keywords: intraionic dyes, merocyanines, zwitterionic dyes, radical polymerization, methylmethacrylate, initiator.

1. Introduction

In the intraionic dyes we have organic cation and anion which are interconnected with the conjugated bonds system [1]. Therefore, the positive and negative charges of both ions are distributed over the chromophore atoms. The total positive charge in intraionic dyes is +1, and the total negative is -1. The presence of two charges, which are equal but opposite in sign, and the possibility of their localization in different parts of the molecule cause the appearance of permanent dipole moment. While for ionic dyes, for example, we can talk only about dipoles of some individual bonds because their molecules are mono-fields. The whole intraionic molecule is electroneutral. Therefore intraionic dyes exist without counterions and they are not “salts-like” compounds. Under electronic excitation due to redistribution of electron density the dipole moment of the dyes (depending on their structure) can both increase or decrease acutely to zero [1]. On this basis intraionic

dyes can be divided into two groups: neutral and zwitterionic dyes.

Neutral intraionic dyes are compounds in which one of the states (primary or excited) can be represented by a neutral frontier structure, and the other one by a bipolar frontier structure. The best examples of such dyes are merocyanines. They are widely used in various light sensitive materials [1, 2]. Since the dipole moment for merocyanines can both increase and decrease, we can distinguish two groups of these compounds, namely merocyanine dyes with positive and negative solvatochromism. If the ground state of the merocyanines is described by a neutral frontier structure and excited state – by a bipolar one, these merocyanines have a positive solvatochromism. It is characterized by a bathochromic shift of the absorption band with the increasing of solvent polarity [3, 4]. Bipolar structure for merocyanines could be also stabilized in the primary state, for example, by introducing groups of strong electron-donating ability in a donor-part of the molecule [3, 4]. Such compounds are called merocyanines with negative solvatochromism and they are characterized by hypsochromic shift of the absorption band with the increasing of solvent polarity [1, 2].



Zwitterionic dyes are organic compounds having bipolar structure both in the main and in the excited states. Typical representatives of these compounds are practically important dyes based on square acid – squarylium dyes [5] and boron-fluoride complexes of pyrromethene [6]. The first dyes due to their high

thermal- and photostability are used as the recording medium for optical laser discs [5]. The last ones have quite rigid structure and as a result are characterized by the high fluorescent ability [6]. Consequently they are widely used as an active laser medium [7].

2. Experimental

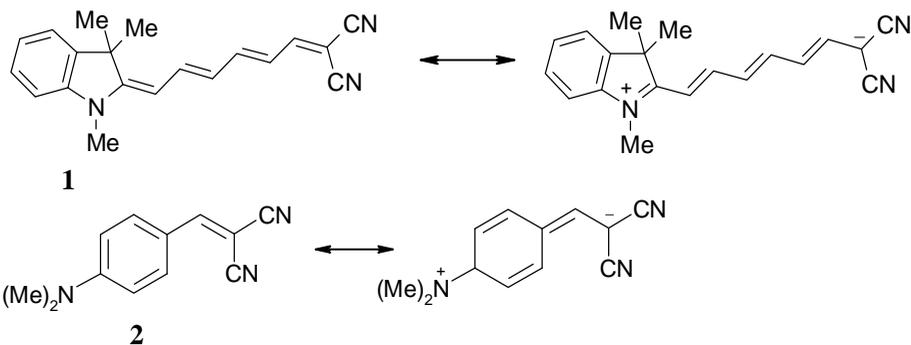
The polymerization ability of MMA DMF solutions in the process of their radical thermoinitiated homopolymerization in the presence of intraionic dyes was investigated by a dilatometry method. Solution of 1.403 mol/l MMA in DMF, that contains 1 % AIBN ($8.43 \cdot 10^{-3}$ mol/l) by mass and the dye DFM solution were carried in the dilatometer with the volume of about 7 ml. The dilatometer was vacuumated, and then filled with argon. The process was repeated three times. The dilatometer was equipped with the thermostatic shirt

(353 ± 0.1 K). Measurements of contractions were carried out within 0.001 mm. Dimensions were conducted with an interval of 1–5 min (depending on the size of contractions). After the last dimension the mass was transferred from the dilatometer to a vessel with silidifier. A polymer was filtered and dried to a permanent mass. The yield of polymer in 3 experiments without addition of dye was normalized, the calculation of the conversion was conducted, calibration kinetic curve was built. Kinetic curves in all of experiments with dyes were built after a calibration curve (using contractions) without determination of formed polymer mass. Using kinetic curves the rate of polymerization (V_g), as a tangent of slope angle of the conversion-time curve on a stationary area, resulted rate of polymerization V_r and total constant of polymerization rate K_{Σ} were determined. The order of the reaction by the initiator was considered to be 0.5 and by a monomer – 1.

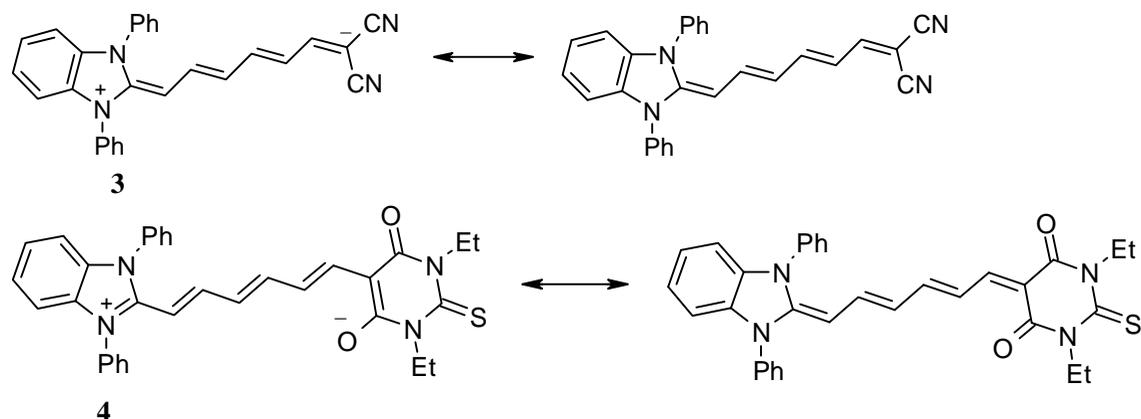
3. Results and Discussion

The objects of our research were:

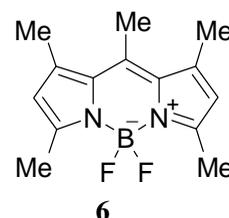
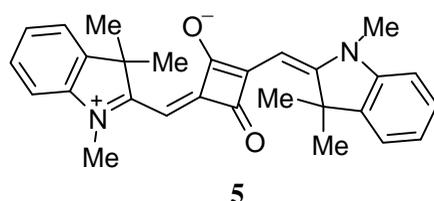
- merocyanines with positive solvatochromism **1** and **2**



- merocyanines with negative solvatochromism **3** and **4**



3) zwitterionic dyes: squarylium dye **5** and borondipyromethene **6**, prevalent under the brand name Pyrromethene PM 546 [3].



In Figs. 1-4 the kinetic curves of thermoinitiated MMA polymerization in DMF solutions with the presence of **1**, **2**, **3**, **4**, **5** and **6** dyes are shown. In Tables 1-2 kinetic parameters of the MMA polymerization processes are represented.

From Fig. 1 it is evident that both merocyanines with positive solvatochromism **1** and **2** (dye concentration is $2 \cdot 10^{-3}$ mol/l) in the presence of AIBN standard initiator serve as inhibitors of the MMA thermal radical homopolymerization in the solution and the reaction rates are $V_g = 1.67 \cdot 10^{-4}$ mol \cdot l $^{-1}$ \cdot s $^{-1}$ and $V_g = 1.63 \cdot 10^{-4}$ mol \cdot l $^{-1}$ \cdot s $^{-1}$ respectively. Without AIBN polymerization process of MMA doesn't occur at all in the presence of both dyes, either **1** or **2**.

From Fig. 2 it is evident that both dyes with negative solvatochromism **3** and **4** in the concentration of $2 \cdot 10^{-3}$ mol/l in the presence of AIBN standard initiator inhibit the MMA thermal radical homopolymerization in the solution. This effect is not significant and the rates of the process are $V_g = 1.70 \cdot 10^{-4}$ mol \cdot l $^{-1}$ \cdot s $^{-1}$ and $V_g = 1.66 \cdot 10^{-4}$ mol \cdot l $^{-1}$ \cdot s $^{-1}$, respectively. Without AIBN polymerization process of MMA doesn't occur at all in the presence of both dyes, either **3** or **4**.

From Figs. 3 and 4 it is evident, that in the presence of AIBN standard initiator dyes **5** and **6** serve as additional initiators of the MMA thermal radical homopolymerization. The highest additional initiation effect is observed for dye **6** ($V_g = 2.26 \cdot 10^{-4}$ mol \cdot l $^{-1}$ \cdot s $^{-1}$); monomer conversion for 195 min was 85 %. The latter statement was confirmed by the fact that this concentration of dye **6** triggers thermal polymerization of MMA (Fig. 4) without a standard initiator AIBN. The process occurs with low rate ($V_g = 0.55 \cdot 10^{-4}$ mol \cdot l $^{-1}$ \cdot s $^{-1}$) and proceeds to the low conversion (15 % for 195 min). The presence of dye **5** in the concentration of $2 \cdot 10^{-3}$ mol/l (Fig. 3) also accelerates the MMA polymerization with the AIBN standard initiator ($V_g = 2.06 \cdot 10^{-4}$ mol \cdot l $^{-1}$ \cdot s $^{-1}$).

MMA polymerization in the presence of **5** or **6** dyes ($2 \cdot 10^{-3}$ mol/l) without AIBN occurs differently. With the first dye (Fig. 4) the process proceeds with a very low rate ($V_p = 0.055 \cdot 10^{-4}$ mol \cdot l $^{-1}$ \cdot s $^{-1}$), rather lower than the MMA polymerization without a dye in the atmosphere of air oxygen. It should be noted that MMA

thermoinitiated polymerization without any initiator in the argon atmosphere does not occur at all. Dye **6** in the concentration of $2 \cdot 10^{-3}$ mol/l initiates MMA polymerization both in the argon and oxygen atmosphere.

Widely accepted opinion was that it is impossible to obtain colored PMMA *via* MMA thermoinitiated polymerization with dyes and without any standard initiator. Invented activity of dyes in this process in the presence of standard initiator is also an untrivial fact, because it was believed they could have an effect only in the presence of some functional groups in their structure, which are able to interact with the initiator. Some of examples could be found in literature, such as for anthraquinone dyes [8].

For zwitterionic dyes the full separation of positive and negative charges to the donor **D** and acceptor **A** fragments could be achieved and they will be conjugated to each other. When we excite the system, including the thermoactivation, the intramolecular electron transfer from the acceptor **A** to the donor **D** can occur. This process should lead to the formation of biradicals (Scheme 1).



Table 1

The kinetic parameters of the thermoinitiated radical homopolymerization of 15 % MMA DMF solutions at 353 K (argon)

Dye	Dye concentration, mol/l	Presence of AIBN, $8.43 \cdot 10^{-3}$ mol/l	$V_g \cdot 10^4$, mol \cdot l $^{-1}$ \cdot s $^{-1}$	$V_r \cdot 10^4$, s $^{-1}$	$K_T \cdot 10^4$, l \cdot mol $^{-1}$ \cdot s $^{-1}$
No dye	0	+	1.84	1.23	5.51
1	$2 \cdot 10^{-3}$	+	1.67	1.19	5.05
2	$2 \cdot 10^{-3}$	+	1.63	1.14	4.97
3	$2 \cdot 10^{-3}$	+	1.70	1.21	5.45
4	$2 \cdot 10^{-3}$	+	1.66	1.18	4.99
5	$2 \cdot 10^{-3}$	+	2.06	1.41	6.00
6	$2 \cdot 10^{-3}$	+	2.26	1.48	6.15

Table 2

The kinetic parameters of the thermoinitiated radical homopolymerization of 15 % MMA DMF solutions at 353 K in different media

Dye	Dye concentration, mol/l (medium)	Presence of AIBN, $8.43 \cdot 10^{-3}$ mol/l	$Vg \cdot 10^4$, $\text{mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$	$Vr \cdot 10^4$, s^{-1}	$K_p \cdot 10^4$, $\text{l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$
No dye	0 (oxygen)	–	0.07	0.04	0.26
5	$2 \cdot 10^{-3}$ (argon)	–	0.055	0.03	0.245
6	$2 \cdot 10^{-3}$ (argon)	–	0.55	0.36	1.59
6	$2 \cdot 10^{-3}$ (oxygen)	–	0.28	0.15	0.82

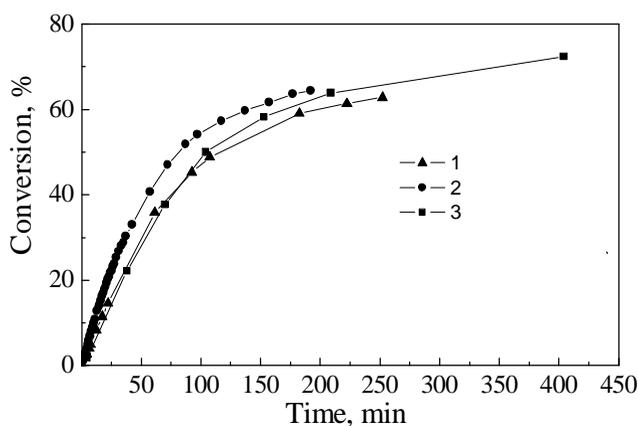


Fig. 1. The kinetic curves of the thermoinitiated radical polymerization of 15 % MMA DMF solutions at 353 K (argon) in the presence of 1 % of AIBN: with $2 \cdot 10^{-3}$ mol/l of 1 (1); without a dye (2) and with $2 \cdot 10^{-3}$ mol/l of 2 (3)

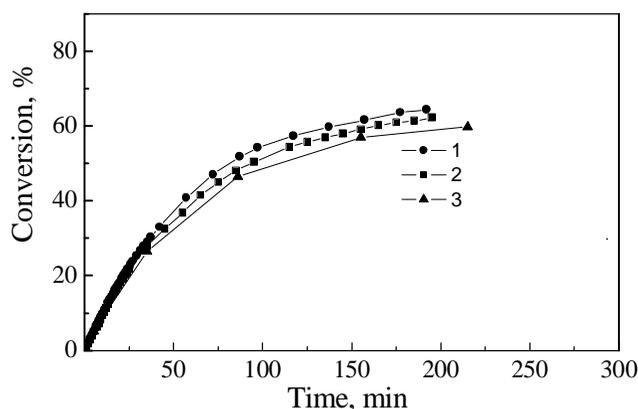


Fig. 2. The kinetic curves of the thermoinitiated radical polymerization of 15 % MMA DMF solutions at 353 K (argon) in the presence of 1 % of AIBN: without a dye (1); with $2 \cdot 10^{-3}$ mol/l of 3 (2) and with $2 \cdot 10^{-3}$ mol/l of 4 (3)

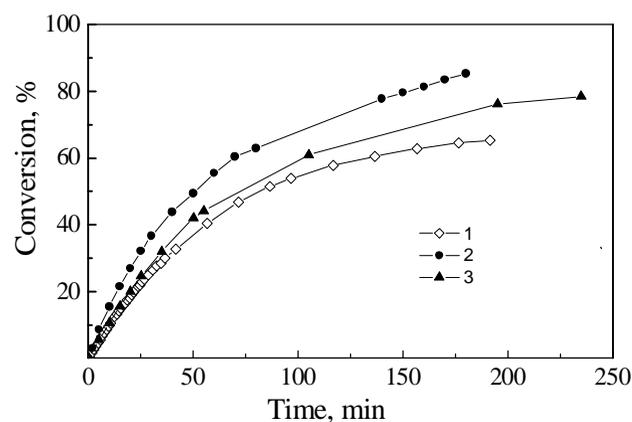


Fig. 3. The kinetic curves of the thermoinitiated radical polymerization of 15 % MMA DMF solutions at 353 K (argon) in the presence of 1 % of AIBN: without a dye (1); with $2 \cdot 10^{-3}$ mol/l of 6 (2) and with $2 \cdot 10^{-3}$ mol/l of 5 (3)

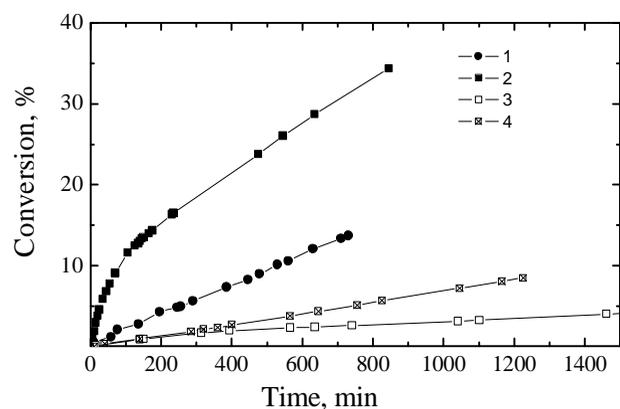


Fig. 4. The kinetic curves of the thermoinitiated radical polymerization of 15 % MMA DMF solutions at 353 K (argon) without AIBN: with $2 \cdot 10^{-3}$ mol/l of 6, oxygen (1); with $2 \cdot 10^{-3}$ mol/l of 6, argon (2); with $2 \cdot 10^{-3}$ mol/l of 5, argon (3) and without a dye, oxygen (4)

The biradical is able to be involved in various types of radical changes, causing the initiation of the MMA polymerization. For example, due to the annihilation of two biradicals the cation- and the anion-radicals could be formed (Scheme 2).



The possibility of biradicals formation for squarylium dyes by the way of their intramolecular charge transfer was observed in work [9].

4. Conclusions

Problems of radical MMA thermopolymerization in the presence of intraionic dyes were investigated. It was shown that the dyes can both inhibit and initiate the polymerization process depending on their electronic

structure. This effect was also observed in the absence of standard initiator AIBN.

The observed initiating ability of dyes **5** and **6** is unusual and practically useful, as it is important for obtaining colored PMMA. Taking into account the chemical and physical properties of dyes **1–6**, we expect that the PMMA coloured with these dyes might find the use as polymers of special application.

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ОСОБЛИВОСТІ ТЕРМОПОЛІМЕРИЗАЦІЇ МЕТИЛМЕТАКРИЛАТУ В ПРИСУТНОСТІ ВНУТРІШНЬОЙОННИХ БАРВНИКІВ

Анотація. Досліджено дилатометричним методом полімеризаційну здатність розчинів метилметакрилату (ММА) у диметилформаміді (ДМФА) в процесі їх радикальної термоініційованої гомополімеризації у присутності внутрішньоїонних барвників. Показано, що барвники можуть ініціювати процес полімеризації в присутності стандартного ініціатора АІБН чи без нього, що є важливим для отримання забарвленого поліметилметакрилату (ПММА).

Ключові слова: внутрішньоїонні барвники, мероціаніни, цвітер-іонні барвники, радикальна полімеризація, метилметакрилат, ініціатор.

