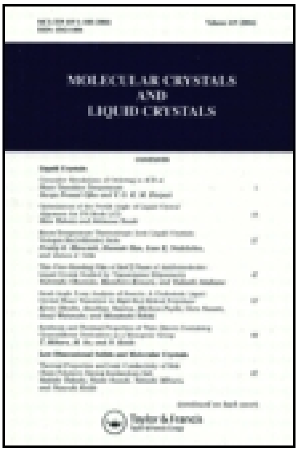

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Effect of a Structure of Polymethine Dyes on the Methyl Methacrylate Free Radical Polymerization in a Solution

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Effect of a Structure of Polymethine Dyes on the Methyl Methacrylate Free Radical Polymerization in a Solution

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The mechanism of running of the MMA thermoinitiated polymerization depending on the chemical structure, ionic nature of polymethine dyes, solvent nature, concentration, temperature, is determined. It is revealed that polymethine dyes are able to initiate, as well as to inhibit, the MMA thermoinitiated free radical polymerization depending on their structure even when the standard initiator is absent. Using quantum chemical calculations, it is found that the initiating ability of polymethine dyes depends on their HOMO energy compared with the same value for the MMA.

Keywords Gravimetry; ionic and intraionic polymethine dyes; kinetics; methyl methacrylate; quantum chemical calculation; thermopolymerization

Introduction

Polymethylmethacrylate (PMMA) has a number of advantages over the other known polymer matrices owing to its good mechanical and optical characteristics, high atmospheric srability, weak absorption, and its low cost. The polymerization carried out in the presence of the dye provides a more uniform dyeing and, accordingly, allows one to get the best parameters of colored PMMA. This method is the most promising and technically applicable. The dyes can take part in the polymerization process chemically. They can react with initiators, take part in the transfer and chain-breakage reactions, and thus influence the polymerization rate, polymer molecular weight, and other polymer characteristics. That is why to get and to analyze some relationship between these reactions and dye's chemical structure is of great interest.

The purpose of this work was to research the influence of the chemical structure and the ionic character of polymethine dyes on the reaction of thermoinitiated polymerization of methylmethacrylate (MMA) in solution. The choice of these dyes

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among all organic dyes is due to the largest range of structural factors and the wide range of photochemical and photophysical properties they have [1–4].

Discussion

Ionic Polymethine Dyes

Cationic Symmetric Polymethine Dyes with Different Lengths of Polymethine Chains. The polymetine chain length influence on the reaction of thermoinitiated polymerization of methylmethacrylate (MMA) in a DMF solution in a series of symmetric polymethine dyes **1**–**3** at different concentrations is investigated. AIBN (1%) was used as an initiator.

From Table 1, it is evident that dye **1** at concentrations of the order of $2 \cdot 10^{-4}$–$1 \cdot 10^{-2}\,\mathrm{mol} \cdot \mathrm{L}^{-1}$ initiates the MMA polymerization. Dye **2** with a longer polymethine chain ($n = 2$) at the same concentrations does not affect the process under selected conditions, but initiates the polymerization at higher concentrations with a low efficiency of initiation. Dye 3 with the longest chain ($n = 3$) at low concentrations does not affect the process, but it inhibits the MMA polymerization at higher concentrations.

The MMA polymerization with dyes **4** and **5** in the absence of a standart initiatior AIBN occurs much more slowly than that with dye **1**. It is of interest that, for these dyes which have the same length of the polymethine chain but different structure of terminal groups than dyes **1**–**3**, we see the reverse trend: namely, with increase in the chain length of a polymethine dye, the initiating capacity increases (Table 1).

Cationic Symmetric Polymethine Dyes with Various Electron-Donating Abilities of Terminal Groups

To investigate the effect of the electron-donating ability of terminal groups for cationic dyes in the MMA polymerization reaction, we chose symmetric dyes 1–9 with the same polymethine chain length, but with different electron-donating abilities of terminal groups. From Table 1, it is evident that, in the presence of AIBN, the electron-donating ability deviates gradually from the average value (dye **1**) both to higher (dye **6**) or lower values (dye **8**), leads initially to the acceleration of the process, but then to its inhibition (dyes **7** and **9**, respectively). In the absence of AIBN, dyes **6, 8,** and **9** also serve as initiators of the polymerization of MMA. It has a tendency to decrease the ability of initiating with increasing the term electron-donating ability of terminal groups in a series of dyes **1**→**6**→**7** and with its decreasing as well (**1**→**8**→**9**). Moreover, dye **7** with strongly electrophilic terminal groups completely loses its initiating ability.

Cationic Polymethine Dyes with Rigidly Fixed Chromophore

It was shown that dye **10** with the polymethine chain fixed by rigidly framed groups, as well as dye **6** (anion-bromide) with a flexible polymethine chain, initiated the MMA polymerization process as in the presence of AIBN and without it (Table 1). This means that the structural rigidity of polymethine dyes is not a prerequisite for initiating the MMA polymerization reaction.

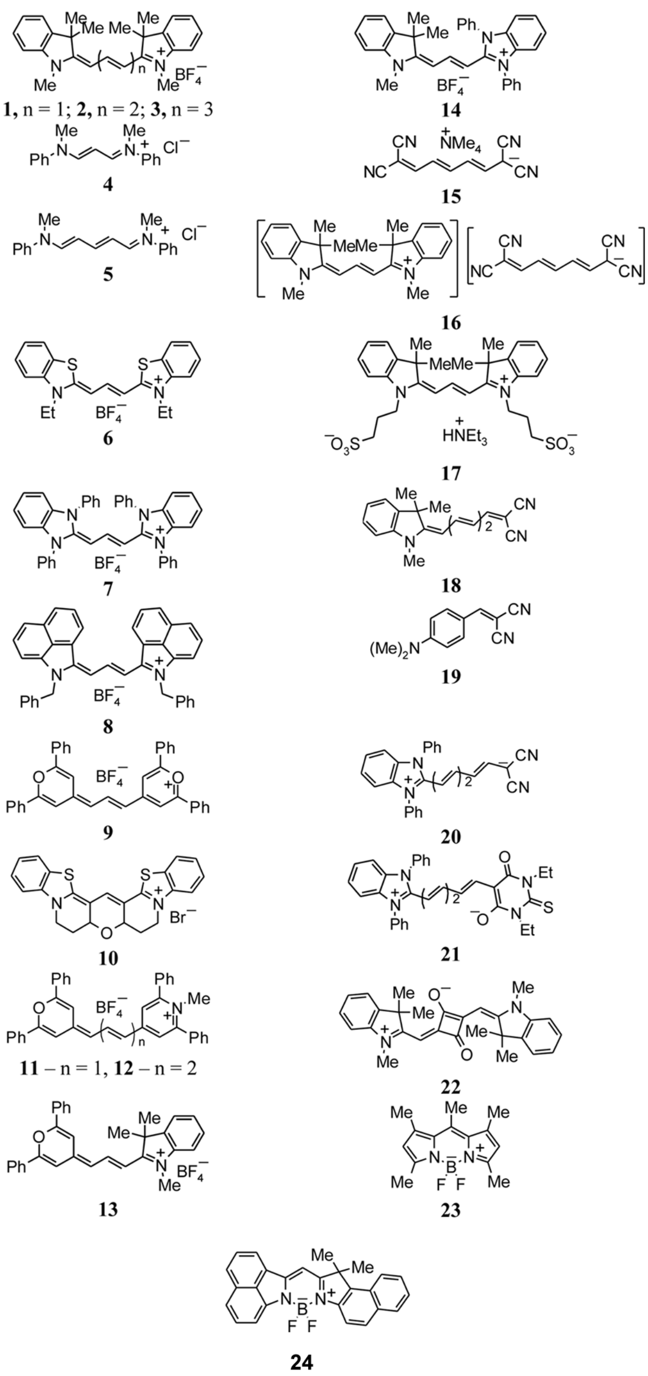

Figure 1. Dyes **1**–**24**.

Table 1. Kinetic parameters of the radical polymerization of 15% MMA with dyes **1–10**, DMF solutions at 80°C (argon)

Dye	Dye conc., $mol \cdot L^{-1}$	AIBN*	$V_g \cdot 10^4$, $mol \cdot L^{-1} \cdot s^{-1}$	$V_r \cdot 10^4$, s^{-1}	$K_\Sigma \cdot 10^4$, $L \cdot mol^{-1} \cdot s^{-1}$	$[\eta]$	M_n
None	0	+	1.84	1.23	5.51	0.40	80600
1	$2 \cdot 10^{-4}$	+	1.81	1.21	5.42	0.40	80600
	$2 \cdot 10^{-3}$	+	2.02	1.35	6.05	0.40	80600
	$1 \cdot 10^{-2}$	+	1.22	0.82	3.67	0.37	72200
	$2 \cdot 10^{-3}$	–	1.00	0.67	3.00	0.43	87150
	$1 \cdot 10^{-2}$	–	1.14	0.75	3.36	0.60	128640
2	$2 \cdot 10^{-4}$	+	1.98	1.33	5.96	0.40	80600
	$6 \cdot 10^{-3}$	+	1.50	0.99	4.59	0.38	74700
	$2 \cdot 10^{-3}$	–	0	0	0	0	0
	$1.3 \cdot 10^{-2}$	–	1.14	0.76	3.40	0.57	123900
3	$2 \cdot 10^{-3}$	+	1.71	1.15	5.15	0.40	80600
	$2 \cdot 10^{-3}$	–	0	0	0	0	0
4	$2 \cdot 10^{-3}$	–	0.29	0.22	1.05	–	–
5	$2 \cdot 10^{-3}$	–	0.43	0.39	1.34	–	–
6	$2 \cdot 10^{-3}$	+	1.92	1.34	5.64	0.40	80600
	$2 \cdot 10^{-3}$	–	0.46	0.30	1.56	0.60	128600
7	$2 \cdot 10^{-3}$	+	1.63	1.12	4.96	0.41	82100
	$2 \cdot 10^{-3}$	–	0	0	0	0	0
8	$2 \cdot 10^{-3}$	+	2.03	1.34	6.03	0.38	74700
	$2 \cdot 10^{-3}$	–	0.43	0.32	1.29	–	–
9	$2 \cdot 10^{-3}$	+	1.80	1.19	5.44	0.40	80600
	$2 \cdot 10^{-3}$	–	0.36	0.25	1.38	–	–
10	$2 \cdot 10^{-3}$	+	2.00	1.33	6.03	–	–
	$2 \cdot 10^{-3}$	–	1.06	0.69	3.01	–	–

*AIBN concentration is $8.43 \cdot 10^{-3} mol \cdot L^{-1}$.

Unsymmetric Cationic Polymethine Dyes with Different Lengths of Polymethine Chain

For strongly asymmetric dyes **11** and **12,** it was found that, as the polymethine chain length increases, the initiating ability of asymmetric cationic dyes decreases. However, for asymmetric dyes, we see a much stronger effect compared with thst for symmetric ones. Without AIBN, the polymerization of MMA in solution does not occur at all, as in the presence of dye **11** and **12**.

Cationic Unsymmetric Polymethine Dyes with Various Electron-Donating Abilities of Terminal Groups

The study of the impact of the electronic asymmetry of dyes on the MMA polymerization is conducted with dyes **11, 13, 14** possessing the same polymethine chain length and different combinations of the electron-donating abilities of terminal groups. It is shown that the emergence of the electronic asymmetry, regardless of a combination of electron-donating abilities, leads to a lower initiating capacity as compared with those of the corresponding symmetric dyes in the presence of the initiator AIBN and to its total loss without AIBN.

Anionic and Cation-Anionic Polymethine Dyes

The influence of anionic dyes on the MMA polymerization is considered to depend on the following factors: the structure of an anionic chromophore; the participation of an anionic chromophore as a colored anion; and the chromophore charge alternation from +1 to −1. To address each of these tasks, we selected respectively the following dyes: **15** – with an anion chromophore, **16** – anion-cation, the hybrid of dyes **1** and **15** with a colored cation and an anion, and **17** – with a cationic chromophore as in dye **1** but with the total charge −1. For comparison, we also examined a mechanical mixture of cationic dye **1** and anionic dye **15**. The process of MMA polymerization with AIBN and dye **15** is slower than that without the dye although the monomer conversion at the same time (195 min) is by 5%. The presence of cation-anionic dye **16** leads to a much faster polymerization. A mechanical mixture of dyes **1** and **15** leads to a greater growth rate of polymerization (V_g) and the monomer conversion as compared with those for dye **16**. The polymerization with dye **17** is almost as fast as without it, although the monomer conversion is lower by almost 10%. In the absence of AIBN, the polymerization of MMA takes place only with dye **17** (Table 2).

Intraionic Polymethine Dyes. Merocyanines

A moderated radical polymerization of MMA in solution is observed for dyes **18** and **19** with positive solvatochromism (the neutral boundary structure dominates in the

Table 2. Kinetic parameters of the radical polymerization of 15% MMA with dyes **1**, **11**–**21** and **1** + **15** ($2 \cdot 10^{-3}$ mol · L^{-1}), DMF solutions at 80°C (argon)

Dye	$V_g \cdot 10^4$, mol · L^{-1} s^{-1}	$V_r \cdot 10^4$, s^{-1}	$K_\Sigma \cdot 10^4$, L · mol^{-1} · s^{-1}
AIBN*	1.84	1.23	5.51
1	2.02 (1.00)	1.35 (0.67)	6.05 (3.00)
11	1.93 (0)	1.25 (0)	5.46 (0)
12	1.71 (0)	1.15 (0)	5.14 (0)
13	1.79 (0)	1.205 (0)	5.32 (0)
14	(0)	(0)	(0)
15	1.79	1.20	5.45
1 + **15**	2.03	1.35	5.95
16	1.90	1.32	5.65
17	1.82 (0.56)	1.22 (0.39)	5.52 (1.65)
18	1.67	1.19	5.05
19	1.63	1.14	4.97
20	1.70	1.21	5.45
21	1.66	1.18	4.99

*AIBN conc. = $8.43 \cdot 10^{-3}$ mol · L^{-1}. In parentheses, we give data obtained in the absence of AIBN.

ground state) and for dyes **20** and **21** with negative solvatochromism (the bipolar structure dominates in the ground state) in the presence of AIBN. None of these dyes did not initiate the polymerization process without AIBN.

Betaine (Zwitterion) Polymethine Dyes

These dyes, unlike merocyanines, retain the bipolar structure both in the ground and excited states. We investigated squarylium dye **22** (a structural analogue of cationic dye **2**) and borondipyrromethene dyes **23** and **24**. The MMA polymerization in the presence of AIBN and dyes **22**–**24** takes place in different ways. At a concentration of $2 \cdot 10^{-3}\,\mathrm{mol} \cdot \mathrm{L}^{-1}$, all the dyes are the additional initiators of the MMA polymerization with the largest effect for dye **23**. Dyes **22** and **24** without AIBN initiate the polymerization, as in an atmosphere of argon and oxygen *, but with a less polymerization rate than that for **23**.

In [5,6], it was found that the initiating ability of polymethine dyes is associated with their possibility to form free radicals. We assume that the formation of radicals can occur as a result of the HOMO and LUMO electrons disconnection through the conversion of vibrational sublevels in molecules. In addition to the thermal population of energy levels, a prerequisite for the electron transfer should be their certain relative position. To determine this location, we have done the quantum-chemical calculations of HOMO and LUMO energies for MMA and all investigated dyes by the AM1 semiempirical method (Table 4).

For well initiating dye **1**, HOMO has a lower energy than the same MMA orbital (Table 4). This means that the released "hole" on the dye HOMO in a pure electronic transition can capture an electron from the MMA HOMO, which will lead to the formation of a neutral radical Dye•. At the same time, MMA will be transformed into cation-radical MMA•$^{+}$. Radical Dye• will begin to initiate the MMA polymerization:

$$\begin{aligned} &\mathrm{Dye}^{\bullet} + \mathrm{MMA} + \cdots + \mathrm{MMA} \rightarrow \mathrm{Dye} - \mathrm{MMA}^{\bullet} \\ &\quad + \cdots + \mathrm{MMA} \rightarrow \mathrm{Dye} - \mathrm{MMA} - \mathrm{MMA}^{\bullet} + \cdots + \mathrm{MMA}. \end{aligned}$$

Table 3. Kinetic parameters of the radical polymerization of 15% MMA with dyes **22–24** ($2 \cdot 10^{-3}\,\mathrm{mol} \cdot \mathrm{L}^{-1}$), DMF solutions at 80°C

Dye (atmosphere)	$V_g \cdot 10^4$, $\mathrm{mol} \cdot \mathrm{L}^{-1}\,\mathrm{s}^{-1}$	$V_r \cdot 10^4$, s^{-1}	$K_\Sigma \cdot 10^4$, $\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{s}^{-1}$
None, (argon)	1.84	1.23	5.51
None, (oxygen)*	0.27	0.18	0.82
22, (argon)	2.06 (0.14)**	1.41 (0.09)	6.00 (0.43)
22, (oxygen)	(0.09)	(0.04)	(0.26)
23, (argon)	2.26 (0.55)	1.48 (0.36)	6.15 (1.59)
24, (argon)	2.08 (0.28)	1.42 (0.18)	6.08 (0.85)
24, (oxygen)	(0.25)	(0.16)	(0.78)

*We mean atmospheric oxygen.

**AIBN conc. = $8.43 \cdot 10^{-3}\,\mathrm{mol} \cdot \mathrm{L}^{-1}$. In parentheses, we give data obtained in the absence of AIBN.

Table 4. HOMO and LUMO energies (E) of dyes **1–15, 18–24** calculated by AM1

Dye	E_{HOMO}, eV	E_{LUMO}, eV
MMA	–10.711	0.341
1	–10.969	–4.649
2	–10.483	–4.675
3	–10.108	–4.688
4	–12.130	–4.467
5	–11.275	–4.556
6	–10.611	–4.744
7	–10.212	–3.880
8	–10.630	–5.051
9	–10.459	–4.842
10	–10.527	–4.702
11	–10.105	–4.422
12	–9.666	–4.409
13	–10.686	–4.814
14	–10.533	–4.128
15	–4.389	1.778
18	–8.095	–1.427
19	–8.540	–1.017
20	–7.946	–1.361
21	–7.955	–1.560
22	–6.862	–2.012
23	–8.002	–1.565
24	–8.016	–1.515

Cation-radical MMA$\bullet^{+}$ can attack the cationic dyes anion An^{-}, leading to the formation of a neutral radical An$\bullet$ and the regeneration of MMA monomeric molecules:

$$\mathrm{MMA}^{\bullet +} + \mathrm{An}^{-} \rightarrow \mathrm{MMA} + \mathrm{An}^{\bullet}$$

At the next step, An$\bullet$ is able to initiate the polymerization of MMA:

$$\begin{aligned} &\mathrm{An}^{\bullet} + \mathrm{MMA} + \cdots + \mathrm{MMA} \rightarrow \mathrm{An} - \mathrm{MMA}^{\bullet} \\ &\quad + \cdots + \mathrm{MMA} \rightarrow \mathrm{An} - \mathrm{MMA} - \mathrm{MMA}^{\bullet} + \cdots + \mathrm{MMA}. \end{aligned}$$

Extending the polymethine chain of symmetric dyes is accompanied by an increase in the HOMO energy (Table 4). Thus, for dye **2** unlike dye **1** with a shorter polymethine chain, it is slightly higher than the MMA HOMO energy. This means that the initiating capacity for dye **2** should decline considerably as compared with dye **1**, which was confirmed by experiment. Since the HOMO of dye **2** has higher energy than the same orbital of MMA, it could not initiate the polymerization. However, the difference between the energies of these orbitals is rather insignificant. As a result, the energy for electron transfer from the MMA HOMO to the HOMO of dye **2** is added by raising the temperature. The further extending of the polymethine chain length

(**2**→**3**) leads to a further increase of the HOMO energy (Table 4). As a result, we have a substantial increase of the energy gap between the HOMO of dye **3** and the MMA HOMO. Therefore, a thermally neutral radical formed from dye **3** loses its initiating ability. Unable to initiate, the dye **3** radical in the presence of AIBN can induce the formation of free radicals. Because of this, dye **3**, unlike similar dyes **2** and **1**, does not initiate the MMA polymerization in the presence of AIBN, but rather inhibits it. Only when dye **3** almost completely disappears, the process of polymerization begins.

The analysis of orbitals shows that the HOMO energy of both dyes, **4** and **5**, unlike compound **2**, is much lower than the MMA HOMO energy. For the last dye, the HOMO energy is more close to that of MMA, as compared with the first one. Therefore, for dyes **4**–**5** in contrast to dyes **1**–**3**, the polymethine chain elongation is accompanied by growing the initiating ability.

A growth of the electron-donating ability of terminal groups in dyes **1, 6**, and **7** leads to growing the HOMO energy (Table 4). For dye **6**, it is a little bit higher than the MMA HOMO energy. This is consistent with a decrease of its initiating capacity. The HOMO energy for dye **7** substantially exceeds that of MMA. For this reason, dye **7** like dye **3** also does not initiate the radical polymerization without AIBN and inhibits the process with it (Table 1).

The terminal groups of dyes **8** and **9**, respectively, are characterized by a weak electron-donating ability. Both dyes, according to their calculated HOMO energies, initiate the polymerization. However, as can be expected from their HOMO "location", they show a weaker initiating ability than that of dye **1**, and it decreases, while passing from dye **8** to compound **9** (Table 2).

The HOMO energy for asymmetric dyes **11**–**14** is significantly higher than the MMA HOMO energy (Table 4). Therefore, these dyes do not initiate its polymerization. Passing from cationic dyes to anionic ones, we have the essential HOMO energy growth (Table 4). This leads to the inactivity and inhibiting ability of anionic polymethine dye **15**, both with and without of AIBN (Table 2). Cation-anionic dye **16** anion is a typical chromophore. Its electronic excitation energy is practically identical with the energy of a chromophore cation of dye **1**. Therefore, it is possible to level the electronic effects in the cation by anion effects. As a result, dye **16** and a mechanical mixture of compounds **1** and **15** also do not initiate the polymerization of MMA, contrary to dye **1**. The calculation results for dye **17** confirm the fact of its activity in the radical polymerization depending on the chromophore structure which is the same as that of dye **1**, but the total charge of the molecule is -1, like that of dye **15**. But, as compared with the last, dye **17** does not initiate the MMA polymerization (Table 2).

Quantum-chemical calculations indicate that the HOMO energy of intraionic polymethine dyes is lower than for the anionic dyes, but significantly higher than for the cationic ones. This is true for dyes with positive (**18** and **19**) and negative (**20** and **21**) solvatochromism. Therefore, they, like the anionic dyes, do not initiate the MMA radical polymerization without AIBN and inhibit it with AIBN (Table 2).

Based on the calculations of HOMO energies, it might be expected that dyes **22**–**24** also should not initiate the MMA polymerization (Table 4). However, in this case, the calculation does not agree with the experiment. All these pigments act as initiators of the polymerization, both with AIBN and without it (Table 3). For these dyes, the complete separation of positive and negative charges is achieved, respectively, for donor and acceptor fragments coupled with one another. At the excitation, the intramolecular electron transfer from an acceptor to a donor can occur. This should lead to the formation of biradicals. The last can be manifested in various types of radical transformations, by entailing the initiation of MMA polymerization.

The ideology developed here of correlation of the energies of dyes and MMA HOMO was successfully used to predict the initiating or inhibitory activity of not only polymethine dyes, but also other classes of organic dyes.

Experimental

Method of Dilatometric Research of the Kinetics of Thermoinitiated Homopolymerization

About 7 ml of a solution of 1.403 mol/l MMA in DMF that contains 1% AIBN ($8.43 \cdot 10^{-3}$ mol/l) by mass and a dye ($2 \cdot 10^{-4}$–$1.3 \cdot 10^{-2}$ mol/l) were carried in a dilatometer by a long thin watering-can. The volume of a dilatometer was evacuated and then filled with argon. A process was repeated three times. The dilatometer is contained in a thermostatted shirt (80 ± 0.1°C). The measurements of contractions were carried out within 0.001 mm. The counting out was conducted with an interval of 1–5 min (depending on the size of contractions). Then the dilatometer content was carried in a vessel with a solidifier. The polymer was filtered and dried to a permanent mass. The yield of the polymer in 3 experiments without addition of a dye was normalized, the calculation of was conversion was conducted, and the calibrating kinetic curve was built. Kinetic curves in all the experiments with dyes were built by the calibrating curve (using contractions) without determination of the polymer mass. Using the kinetic curves, the speed of polymerization (V_g) is determined, as the inclination angle tangent of the conversion – time curve on a stationary segment. The resulted speed of polymerization V_r and the total constant polymerization speed $K_{\sum}$ were also determined from kinetic curves. The order of the reaction by an initiator was considered 0.5, and that by a monomer was 1.

Determination of the Average Viscosimetric Molecular Mass of PMMA

Polymers which appeared in all the experiments were purified by the triple solidification from ethylacetate into isopropanole. The polymers were dried in vacuum, and then their molecular mass and the spectra of absorption were determined. The viscosimeter was contained in a thermostatted shirt (25 ± 0.1°C). Into the viscosimeter, 7 ml of chloroform were placed. After 10–15 min of the thermal control, we measured the outflowing time of chloroform (τ_0) and then the preliminary prepared solutions of polymer 4 at the known concentrations (τ). The values of characteristic viscosity were determined on the axis of ordinates, where we took a segment with a linear dependence of η on the polymer solution concentration C (g/100 ml). It is considered that the specific viscosity (η) is numerically equal to $\tau/\tau_0 - 1$. The molecular mass of PMMA was calculated by the formula $\lg M = \lg[\eta] - \lg K/\alpha$.

Conclusions

We have determined the mechanism of MMA thermoinitiated polymerization, depending on the chemical structure, ionic nature of polymethine dyes, solvent nature, concentration, and temperature.

It is revealed that polymethine dyes, depending on their structure, are able to initiate, as well as to inhibit, the MMA thermoinitiated free radical polymerization even when a standard initiator is absent.

It is shown that the highest occupied molecular orbital (HOMO) of a dye has to have a lower energy than an analogous orbital of MMA, so that the free radical is produced. It is determined that the HOMO energy of the cationic polymethines grows in the following cases: the polymethine chain lengthens, electron-donor ability of the terminal groups deviates from the average one, and the electron asymmetry increases. That leads to a reduction of the initiating ability of the cationic dyes under such changes of their chemical structure. The HOMO energy of anionic and intraionic merocyanic dyes with positive and negative solvatochromism is shown to be much higher than that in the case of cationic dyes and exceeds the MMA HOMO energy. Hence, they do not initiate the MMA free radical polymerization.

Intraionic squarylium and borondipyrromethene dyes are weak initiators of the MMA polymerization both in the presence of the initiator and in its absence, despite the fact that they have higher HOMO energies than that of MMA. The formation of biradicals due to the electron transfer from the acceptor part of a molecule to the donor one is assumed in this case.

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