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Effect of Polymethine Dyes with Various Electron-Donating Abilities of Terminal Groups on Thermopolymerization of Methylmethacrylate in Solutions

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The process of radical thermo-initiated polymerization of DMF (dimethylformamide) MMA (methylmethacrylate) solutions is investigated kinetically. It is shown that the reaction occurs in the presence of symmetric cation polymethine dyes containing terminal groups of strong, moderate, and weak electron-donating abilities. It is established that, with growing the terminal group electron-donation, an increase of the monomer conversion occurs at the same reaction times. Using DFPH (diphenylpicrylhydrazyl), it is shown that the process is to be considered as a radical one.

Keywords: initiator; polymethine dyes; radical polymerization

INTRODUCTION

Polymeric materials which possess uniform color and specified optical-mechanical properties and resistant to light and other natural factors are essential for the formation of active [1] and passive [2] laser media, as well as for the production of protective light filters [3] in quantum electronics [4], luminescent solar convectors [5] in solar power engineering and space exploration [6], etc.

Coloration of PMMA (polymethylmethacrylate) is a challenging perspective task owing to remarkable optical and mechanical properties

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of this polymer. It allows the creation of materials characterized by high-grade optical properties through a mechanical treatment [7].

Polymethine dyes are of greatest interest to this task, as they possess unique properties regarding the optical energy transformation [8,9] and therefore are widely used in laser media [4], optical information recording media, electroluminescent displays, photovoltaic devices, etc. [10]. However, their behavior in MMA radical polymerization processes depending on the electron structure was not investigated.

EXPERIMENTAL

1. Method of Dilatometric Research of the Kinetics of Thermoinitiated Polymerization

A solution of 1.403 mole/l MMA in DMF that contains 1% AIBN ($8.43 \cdot 10^{-3}$ mole/l) by mass and dye **1–3** ($2 \cdot 10^{-3}$ mole/l) was carried by a long thin watering-can into a dilatometer with a volume of about 7 ml. A dilatometer was vacuumized and then filled with argon. The process was repeated three times. A dilatometer was contained in a thermostat (80 ± 0.1°C). The measurement precision is within 0.001. Counting out was conducted in a time interval of 1–5 min (depending on the size of contractions). After the last counting out, the content of a dilatometer was carried into a vessel with solidifier. A polymer was filtered and dried to a permanent mass. The yield of a polymer in 3 experiments without addition of dye is normalized, the calculation of the conversion is performed, and the calibration kinetic curve is constructed.

Kinetic curves in all experiments with dyes were constructed after the calibration (using contractions) without determination of the mass of a polymer appeared. Using the kinetic curves, the rate of polymerization (V_g) was determined as the inclination angle tangent of the conversion – time curve on a stationary section, resulted rate of polymerization V_r, and total rate of polymerization $K_{\sum}$. The order of the reaction was considered to be 0.5 by an initiator and 1 by a monomer.

2. Determination of the Average Viscosimetric Molecular Mass of PMMA

Polymers which appeared in all of the experiments were purified by triple solidification from ethylacetate into isopropanol. The polymers dried up in vacuum were utilized for the determination of their molecular mass and the absorption spectra. A viscosimeter was contained in a thermostat (25 ± 0.1°C). In a viscosimeter, we placed 7 ml of

chloroform. In 10–15 min of the thermostatic control, we measured the outflowing time of chloroform (t_0) and then those of preliminarily prepared solutions of the polymer (t). The values of characteristic viscosity were determined by a segment on the axis of ordinates which is cut by the curve η versus the polymer solution concentration C (in g/100 ml). The specific viscosity η was numerically equal to $t/t_0 - 1$. The molecular mass of PMMA was calculated by the formula lg $M = \lg[\eta] - \lg K/\alpha$.

3. Absorption Spectra

The absorption spectra of dyes and DFPG solutions were measured in DMF on a Shimadzu UV-3100 spectrophotometer at 293 K in quartz cuvettes of 1 cm in thickness in the range of wavelengths of 350–850 nm.

RESULTS AND DISCUSSION

In our previous investigations, we have established the patterns of the MMA radical polymerization in the presence of polymethine dyes having various polymethine chain lengths [11]. Symmetric polymethine dyes **1–3** having the same polymethine chain length but different electron-donating abilities of terminal groups [moderate (**1**), strong (**2**), and weak (**3**) [12]] were used in further investigations. Dyes 1–3 are cationic. The total charges of their chromophores in the ground and excited states equal +1. The uniformity of the charge distribution on chromophore atoms is determined by the electron-donating ability [of the (heterocycle's) terminal groups]. A positive charge of the dyes with groups of high electron-donating ability was localized mostly on heterocycles, whereas it was localized on polymethine chains in the case of dyes with weak electron-donating ability. The greatest uniformity of the charge distribution between a heterocycle and a chain was observed for dyes with moderate electron-donating ability of the terminal groups (Fig. 1).

The kinetics of radical thermoinitiated polymerization of MMA in the presence of dyes **1–3** was studied by dilatometry. A process was carried out in a 15% solution of DMF at 80°C in the argon atmosphere. AIBN (azobisisobutyronitrile) was used as an initiator (1%). Contractions were determined by a KM-6 cathetometer. The conversion degree in 3 experiments without dyes was measured using the gravimetric analysis. Due to the identical experimental conditions (the temperature was the same, as well as the monomer concentration in the identical solvent), the data obtained were averaged out, and the

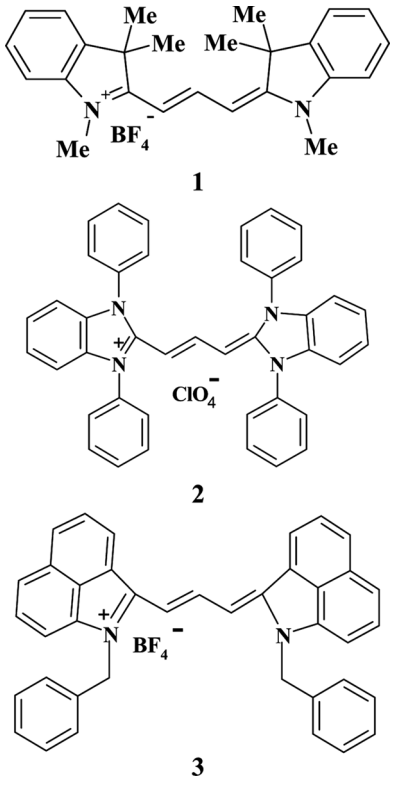

FIGURE 1 Objects of the research.

kinetic curve was traced. Kinetic curves for further experiments were traced using the calibration curve without mass determination of the polymer obtained.

The kinetic curves of radical polymerization of MMA in the presence of 1% of AIBN and dyes **1–3** are shown in Figure 2 and Table 1. The kinetic parameters of this process were calculated after the kinetic curves of polymerization of MMA were obtained. As the concentrations of a monomer and an initiator in the experiments were identical, it is possible in the comparison of polymerization activities to use the values of growth rate on the stationary sections of kinetic curves.

Figure 2 and Table 1 show that the MMA polymerization in the presence of a standard initiator (1% AIBN) as well as in the presence of dyes **1–3** of the same concentrations ($2 \cdot 10^{-3}$ mole/l) goes in different ways. Dyes **1** and **2**, having terminal groups of moderate and strong

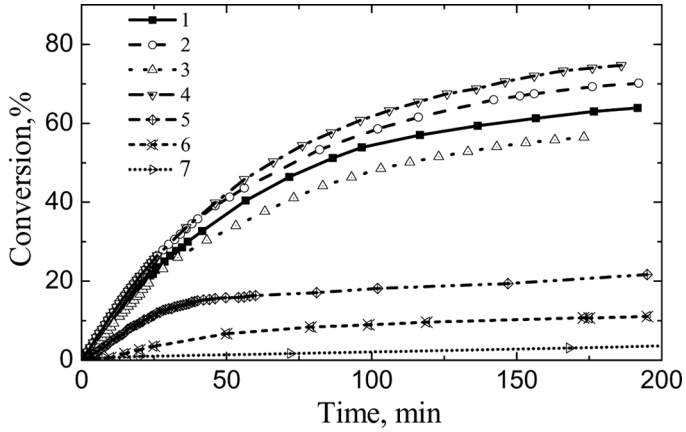

FIGURE 2 Kinetic curves of the radical polymerization of 15% MMA DMF solutions at 80°C (argon) with 1% of AIBN: 1 – without dye, 2 – with $2 \cdot 10^{-3}$ mole/l **1**, 3 – with $2 \cdot 10^{-3}$ mole/l **3**, 4–with $2 \cdot 10^{-3}$ mole/l **2**, and without AIBN: 5 – with $2 \cdot 10^{-3}$ mole/l **1**, 6 – with $2 \cdot 10^{-3}$ mole/l **2**.

electron-donating abilities, respectively, serve as initiators of the MMA polymerization process ($V_g = 2.03 \cdot 10^{-4}$ and $2.02 \cdot 10^{-4}$ $\text{mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$). In this case, the monomer conversion during 195 min was 75 and 70%, respectively. The last assumption confirms the initiation of the MMA polymerization process (curves 5, 6) by dyes 1 and 2 in the indicated concentrations without AIBN application. The processes run at low rates ($V_g = 1.00 \cdot 10^{-4}$ and $0.43 \cdot 10^{-4}$ $\text{mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$) and up to insignificant conversions (22% and 12% during 195 min). Dye **3** containing terminal groups with weak electron-donating ability

TABLE 1 Kinetic Parameters of the Radical Polymerization of 15% MMA DMF Solutions at 80°C (argon)

Dye	Dye conc. ($\text{mol} \cdot \text{L}^{-1}$)	AIBN*	$V_g \cdot 10^4$ ($\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$)	$V_r \cdot 10^4$ (s^{-1})	$K_\Sigma \cdot 10^4$ ($\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)	$[\eta]$	M_n
None	0	+	1.84	1.23	5.51	0.40	80600
1	$2 \cdot 10^{-3}$	+	2.02	1.35	6.05	0.40	80600
	$2 \cdot 10^{-3}$	–	1.00	0.67	3.00	0.43	87150
3	$2 \cdot 10^{-3}$	+	1.63	1.12	4.96	0.41	82100
	$2 \cdot 10^{-3}$	+	2.03	1.34	6.03	0.38	74700
2	$2 \cdot 10^{-3}$	–	0.43	0.32	1.29	–	–

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

under the same conditions inhibits the polymerization process ($V_g = 1.63 \cdot 10^{-4} \text{mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$, the conversion is 55% during 195 min).

The data shown allow us to make an assumption that dyes **1–3** under thermopolymerization conditions are able to form free radicals which can serve in the reaction both as initiators and inhibitors. The average molecular mass of the polymers was determined using viscosimetry (VPJ-1 mark) data at (25±0.1°C) in chloroform solutions. The corresponding values of molecular masses are graphically given in Table 1 (Table 1). The values of molecular masses of PMMA confirm the idea

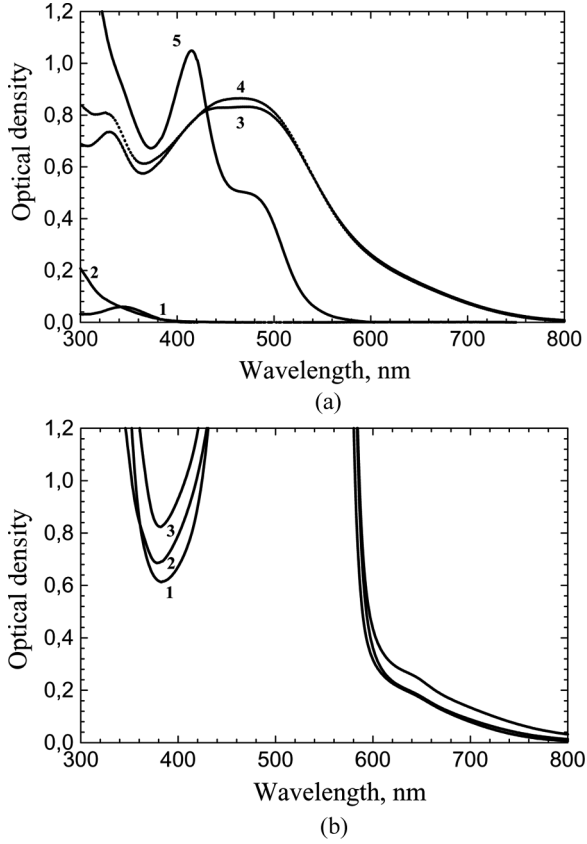

FIGURE 3 (a) Absorption spectra of: **1**+**DFPH** – 1, **1**+**DFPH** heated during 40 min at 80°C – 2, **1**+**DFPH** heated during 60 min at 80°C – 3 (DMF); (b) Absorption spectra of: **AIBN** – 1, **AIBN** heated during 180 min under 80°C – 2, **DFPH** – 3, **DFPH** heated during 180 min at 80°C – 4, **AIBN**+**DFPH** heated during 180 min at 80°C – 5 (DMF).

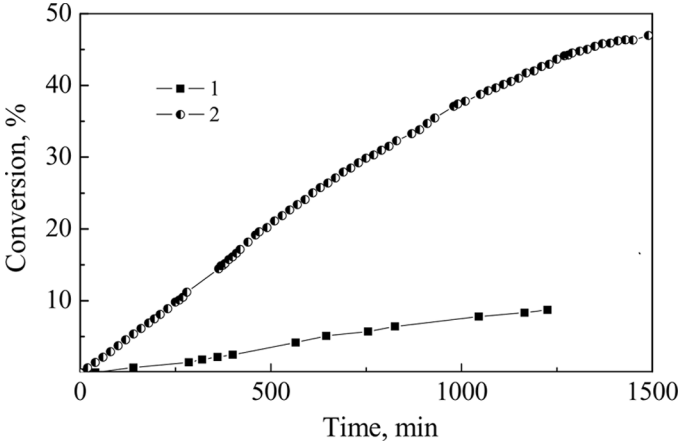

FIGURE 4 The kinetic curves of the radical polymerization of 15% MMA DMF solutions at 80°C (oxygen): 1 – without dye, 2 – with $2 \cdot 10^{-3}$ mole/l **1**.

of that dyes **1** and **2** are the initiators of the radical polymerization. Dye **3** in the same concentration is an inhibitor of the process of radical thermoinitiated polymerization of MMA. The difference between the values of final PMMA molecular masses and those from the standard experiment without dye allows us to exclude the ionic reaction mechanism, because the masses differ very significantly. To prove the radical mechanism of MMA thermopolymerization under the influence of polymethine dyes **1–3**, we have studied these reactions in the presence of DFPH known as a trap of radicals, which has characteristic lines in the electronic absorption spectrum. It can be seen from Figure 3 and 3b that such lines appear at 380 and 420 nm. It is worth noting that the MMA polymerization with DFPH does not result in the appearance of these lines at 380 nm in the absence of dyes.

It is known that oxygen under certain conditions during the interaction with dyes gives rise to free radicals [13] initiating the polymerization process. We have studied the MMA polymerization in the oxygen atmosphere under the same conditions as those in the argon atmosphere. By the example of dye 1 (Fig. 4), it is clear that polymethine dyes are able to initiate the polymerization process in the oxygen atmosphere and without AIBN and give rise to free radicals.

CONCLUSIONS

The dependence of the MMA polymerization in a DMFA solution in the presence of AIBN, as well as dyes 1–3, on the electron-donating

activity of terminal groups is shown. An increase of the electron-donating ability from weak to strong (**1** → **2**) one increases the initiating ability. *Vice versa*, a decrease of the electron-donating ability of terminal groups (**1**→**3**) leads to inhibiting the process by the dye. The MMA polymerization in a solution in the presence of dyes **1**–**3** was proved to run due to the radical mechanism. The above-mentioned mechanism exists both in the absence of the initiators and atmospheric oxygen.

REFERENCES

[1] Bezrodnyi, V. I. & Ishchenko, A. A. (2001). *Appl. Phys. B.*, *73*, 283.
[2] Bezrodnyi, V. I. & Ishchenko, A. A. (2002). *Optics and Laser Technology*, *34*, 7.
[3] Bezrodnyi, V. I., Derevyanko, N. A., Ishchenko, A. A., Karabanova, L. V., Plisko, T. A., Slominskii, Yu. L., & Smirnova, A. L. (1996). *Optical Technology*, *63*, 936.
[4] Ishchenko, A. A. (1994). *Quantum Electronics*, *24*, 471.
[5] Ishchenko, A. A. (1991). *Russian Chemical Reviews*, *60*, 865.
[6] Ishchenko, A. A. (1991). *Journal of Applied Spectroscopy*, *55*, 1057.
[7] *Functional Organic Materials. Syntheses, Strategies and Applications* (Edited by Thomas J. J. Müller and Uwe H. F. Bunz). *Wiley-VCH*: Weinheim, Vol. 1 (2007). KGaA, *1*, 590.
[8] Bach, G. & Daehne, S. (1997). Cyanine dyes and relited Compunds In: *Rodd's Chemistry of Carbon Compounds, IVB Heterocyclic Compounds*, Sainsbury, M. (Ed.), Elsevier: Amsterdam, p. 383–481.
[9] Mishra, A., Behera, R. K., Behera, P. K., Mishra, B. K., & Behera, G. B. (2000). *Chem. Rev.*, *100*, 1741.
[10] Davidenko, N. A., Ishchenko, A. A., & Kuvshynskiy, N. G. (2005). *Photonics of Molecular Semiconductor Composites on the Basis of Organic Dyes*, Naukova Dumka: Kyiv (in Russian).
[11] Grabchuk, G. P., Ishchenko, A. A., & Kolendo, A. Yu. (2008). *Mol. Cryst. Liq. Cryst.*, *485*, 69/[817].
[12] Ishchenko, A. A. (1994). *Structure and Spectral Luminescent Properties of Polymethine Dyes*, Naukova Dumka: Kyiv (in Russian).
[13] Songjie Yang, He Tian, Heming Xiao, Xinghong Shang, Xuedong Gong, Side Yao, & Kongchang Chen. (2001). *Dyes and Pigments*, *49*, 93.