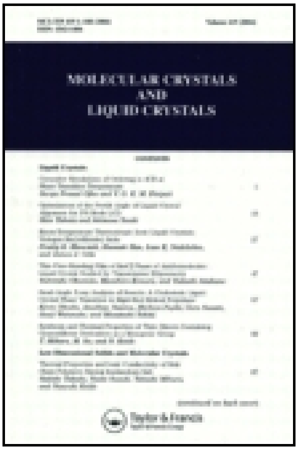


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Influence of Cationic Symmetric Polymethine Dyes on Radical Polymerization of Methylmethacrylate in Solution

G. P. Grabchuk [a], A. A. Ishchenko [a] & A. Yu. Kolendo [a]

[a] Polymer Chemistry Department, Kiev National Taras Shevchenko University, Kiev, Ukraine

To cite this article: G. P. Grabchuk, A. A. Ishchenko & A. Yu. Kolendo (2008): Influence of Cationic Symmetric Polymethine Dyes on Radical Polymerization of Methylmethacrylate in Solution, Molecular Crystals and Liquid Crystals, 485:1, 817-824

To link to this article: http://dx.doi.org/10.1080/15421400801918195

Mol. Cryst. Liq. Cryst., Vol. 485, pp. 69/[817]–76/[824], 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801918195

Taylor & Francis
Taylor & Francis Group

Influence of Cationic Symmetric Polymethine Dyes on Radical Polymerization of Methylmethacrylate in Solution

G. P. Grabchuk, A. A. Ishchenko, and A. Yu. Kolendo
Polymer Chemistry Department, Kiev National Taras Shevchenko University, Kiev, Ukraine

The polymerization ability of methylmethacrylate solutions in DMF and toluene in the process of their radical thermoinitiated homopolymerization in presence of polymethine dyes is investigated, utilizing dilatometry method. Conformities to the law of influencing of these dyes, depending on length of polymethine chain and concentrations are obtained.

Keywords: initiator; polymethine dyes; radical polymerization

INTRODUCTION

The synthesis of the colored polymers with adjusted properties is among the most significant tasks of modern polymer chemistry. Such compounds have found wide application in laser techniques, data management devices, helioenergetics and optoelectronics, they have a number of advantages in comparison to liquid colored materials, having easier build, lesser toxicity and the capability to work with in the conditions of extreme temperatures.

The polymerization was carried out in presence of the dye provides more uniform dyeing and solid bonding. This method is the most promising and technically applicable. The dyes can take part in the polymerization process chemically, which can be either good or unlikely [1–7]. The study of the influence of the dye on such processes, met in the literature, is insufficient.

Address correspondence to G. P. Grabchuk, Polymer Chemistry Department, Kiev National Taras Shevchenko University, Volodymyrska Str. 64, Kiev 01033, Ukraine. E-mail: grabchyk2004@mail.ru

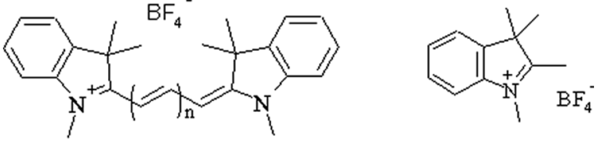
The problem of polymethylmethacrylate (PMMA) is significant, as this polymer has good mechanical and optical characteristics, which permit to synthesize the materials with interesting optical properties [1–7]. What is also convenient, the properties of PMMA can be predictably varied by plastification. Thus, it is possible to avoid such effects, as aggregation of dyes, anisotropy of optical properties of standards [8], etc. That is why the purpose of this work was to research the influence of cationic symmetric polymethine dyes on the reaction of polymerization of methylmethacrylate (MMA) in solution.

DISCUSSION

A number of polymethine dyes, which are widely used in quantum electronics, optoelectronics, as active laser environments was used for the research [5, 9]. Namely, indopolycarbocyanine dyes **(I)–(III)**, and also organic salt, which is the component part of eventual heterocyclic groups of these dyes **(IV)** [10]:

The kinetics of radical thermo initiated homo polymerization of MMA in presence of dyes **(I)–(III)** was studied by dilatomety method. A process was carried out in a 15% solution of DMF at 80°C in the argon atmosphere. AIBN (1%) was used as an initiator. Contractions were determined by KM-6 kathetometer. Degree of conversion in 3 experiments without dyes was measured using gravimetric analysis. Due to the identical experimental conditions (temperature was the same, as well as monomer concentration in the identical solvent) data obtained were averaged out and kinetic curve was traced. Kinetic curves for further experiments were traced using calibration curve with no mass determination of the polymer obtained.

The kinetic curves of radical homopolymerization of MMA in presence of dyes **(I)–(III)** are shown on Figure 1, and in a Table – the kinetic parameters of this process, were calculated after the kinetic curves of homopolymerization of MMA were obtained. As concentrations of monomer and initiator, in the experiments were identical,



(I) - n = 1, (II) - n = 2, (III) - n = 3

SCHEME 1 Indopolycarbocyanine dyes (I)–(III), salt (IV), used for the polymerization.

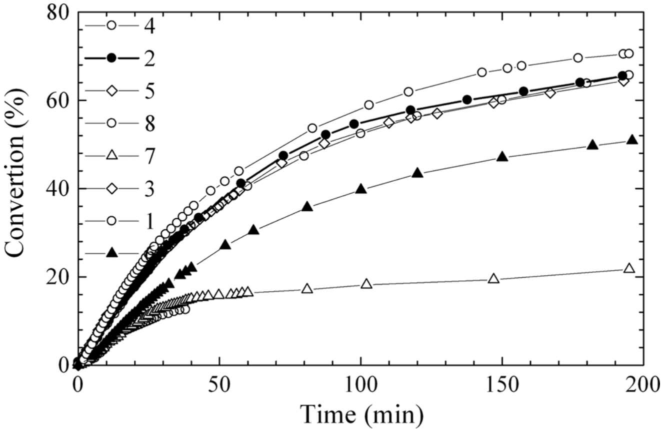


FIGURE 1 The kinetic curves of the radical polymerization of 15% MMA DMF solutions at 80°C (argon) with 1% of AIBN: 1 – with $2 \cdot 10^{-3}$ mol/L **(I)**, 2 – without a dye, 3 – with $2 \cdot 10^{-4}$ mol/L **(I)**, 4 – with $21 \cdot 10^{-3}$ mol/L **(III)**, 5 – with $2 \cdot 10^{-4}$ mol/L **(III)**, 6 – with $1 \cdot 10^{-2}$ mol/L **(I)**, and without AIBN: 7 – with $2 \cdot 10^{-3}$ mol/L **(I)**, 8 – with $1.3 \cdot 10^{-2}$ mol/L **(II)**.

for comparison of polymerization activity it is possible to use the values of speed of growth on the stationary areas kinetic curves.

From Figure 1 it is evident, that homopolymerization of MMA in presence, of dye **(I)** depending on its concentration takes place in different way. Thus, in a concentration $2 \cdot 10^{-4}$ M in presence of AIBN dye **(I)** has no influence on the speed of process of polymerization of MMA ($Vg = 1.84 \cdot 10^{-4}$ $mol \cdot l^{-1} \cdot s^{-1}$) and conversion of the monomer (64% after 195 min) and kinetic curves 2 and 3 coincide practically. After concentration was increased in 10 times (up to $2 \cdot 10^{-3}$ M) speed of process of polymerization of MMA increased as well ($Vg = 2.02 \cdot 10^{-4}$ $mol \cdot l^{-1} \cdot s^{-1}$) and the conversion of the monomer after 195 min was 70% (curve 1). We suppose, that in this concentration dye **(I)** serves as the additional initiator of the process. The last idea confirms the fact that in this concentration, but without AIBN, dye **(I)** initiates the process of polymerization of MMA indeed (curve 7). A process takes place with a small speed ($Vg = 1.00 \cdot 10^{-4}$ $mol \cdot l^{-1} \cdot s^{-1}$) and passes to insignificant conversions (22% after 195 min). At the concentration increased as in previous case at 10 times (up to $1 \cdot 10^{-2}$ mol/l) dye **(I)** retards the process of polymerization of MMA ($Vg = 1.22 \cdot 10^{-4}$ $mol \cdot l^{-1} \cdot s^{-1}$) and the conversion up to the 51% after 195 min (curve 6).

Presence of dyes **(II)** and **(III)** in concentrations $2 \cdot 10^{-4}$ mol/l (curve 5) and $2 \cdot 10^{-3}$ mol/l (curve 4) during the polymerization of MMA in presence of AIBN similar to dye **(I)** practically has no influence on the speed of process – ($Vg = 1.98 \cdot 10^{-4}\,mol \cdot l^{-4} \cdot s^{1}$ and $Vg = 1.71 \cdot 10^{-4}\,mol \cdot l^{-1} \cdot s^{-1}$ accordingly) and conversion to the monomer and their kinetic curves practically coincide with the kinetic curve of polymerization of MMA without addition of the dye.

Dye **(II)** is the initiator of polymerization MMA with no use of AIBN, but in a considerably greater concentration as compared to dye **(I)** ($1{,}3 \cdot 10^{-2}$ mol/l) ($Vg = 1.14 \cdot 10^{-4}\,mol \cdot l^{-1} \cdot s^{-1}$).

Polymerization of MMA in presence of $2 \cdot 10^{-3}$ mol/l of dye **(III)** and absence, of AIBN does not take a place at all.

Dyes, utilized by us for research are of cationic type and are salts. To check up the possibility of existence of specific influence on the process of radical polymerization of organic salts, the process of radical thermoinitiated polymerization of MMA was probed in solution of DMF in the presence of AIBN and also in the presence of l,3-trimethyl-3-H-indolium **(IV)**, which is the component part of terminal groups of dyes **(I)–(III)** with the same anion. As can be seen from curves 4, presence of salt (IV) in concentrations $2 \cdot 10^{-3}$ mol/l (curve 2) and $8 \cdot 10^{-3}$ mol/l (curve 3) during polymerization of MMA in presence of AIBN has no influence on the speed of the process – ($Vg = 1.82 \cdot 10^{-4}\,mol \cdot l^{-1} \cdot s^{-1}$ and $Vg = 1.81 \cdot 10^{-4}\,mol \cdot l^{-1} \cdot s^{-1}$ accordingly) and conversion of the monomer (unlikely to dyes **(II)–(III)**) and their kinetic curves practically coincide with the kinetic curve of polymerization of MMA without addition of dye.

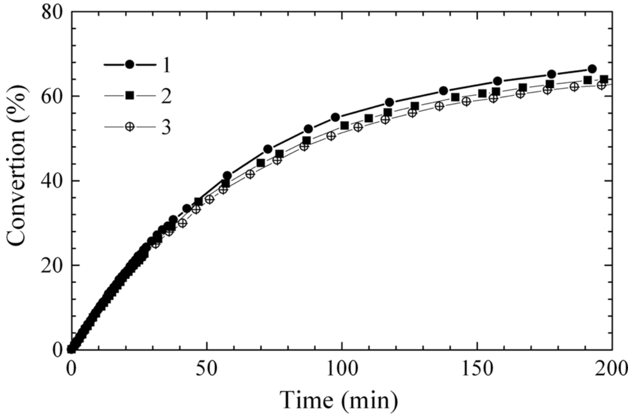


FIGURE 2 The kinetic curves of the radical polymerization of 15% MMA DMF solutions at 80°C (argon) with 1% of AIBN: 1 – without a dye, 2 – with $2 \cdot 10^{-3}$ mol/L **(IV)**, 3 – with $8 \cdot 10^{-3}$ mol/L **(IV)**.

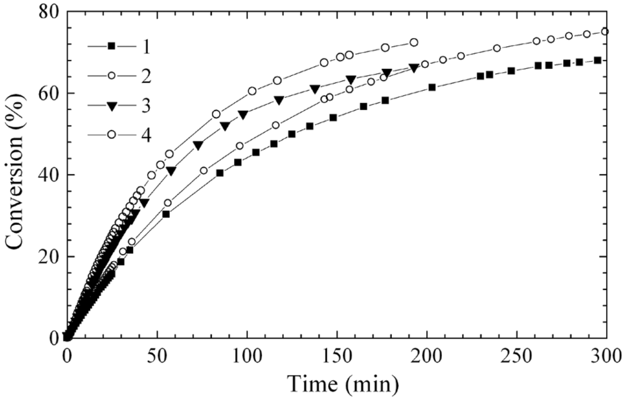


FIGURE 3 The kinetic curves of the radical polymerization of 15% MMA solutions at 80°C (argon) with 1% of AIBN: 1 – without a dye in toluene, 2 – with $2 \cdot 10^{-3}$ mol/L **(I)** in toluene, 3 – without a dye in DMF, 4 – with $2 \cdot 10^{-3}$ mol/L **(I)** in DMF.

On Figure 3 the kinetic curves of radical homopolymeriztion of MMA are resulted in presence of dye **(I)** in a concentration $2 \cdot 10^{-3}$ mol/l in the presence of AIBN and homopolymerization of MMA without dye in presence of AIBN in different solvents. Namely, in unpolar toluene, in which theese dyes exist as contact, ionic pair, and in strongly polar DMF, in which they are fully dissociated. Other terms of experiment are unvaried. From the figure it is evident, that

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

Dye	Dye conc. ($\mathrm{mol} \cdot \mathrm{L}^{-1}$)	AIBN*	$V_g \cdot 10^4$ ($\mathrm{mol} \cdot \mathrm{L}^{-1} \cdot \mathrm{s}^{-1}$)	$V_r \cdot 10^4$ (s^{-1})	$K_\Sigma\ 10^4$ ($\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{s}^{-1}$)	[η]	M_n
None	0	+	1.84	1.23	5.51	0.40	80600
(I)	$2 \cdot 10^{-4}$	+	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
(II)	$2 \cdot 10^{-4}$	+	1.98	1.33	5.96	0.40	80600
	$1.3 \cdot 10^{-2}$	–	1.14	0.76	3.40	0.57	123960
(III)	$2 \cdot 10^{-3}$	+	1.71	1.15	5.15	0.40	80600
	$2 \cdot 10^{-3}$	–	0	0	0	0	0
(IV)	$2 \cdot 10^{-3}$	+	1.82	1.22	5.45	0.47	97400
(IV)	$8 \cdot 10^{-3}$	+	1.81	1.21	5.43	0.47	97400

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

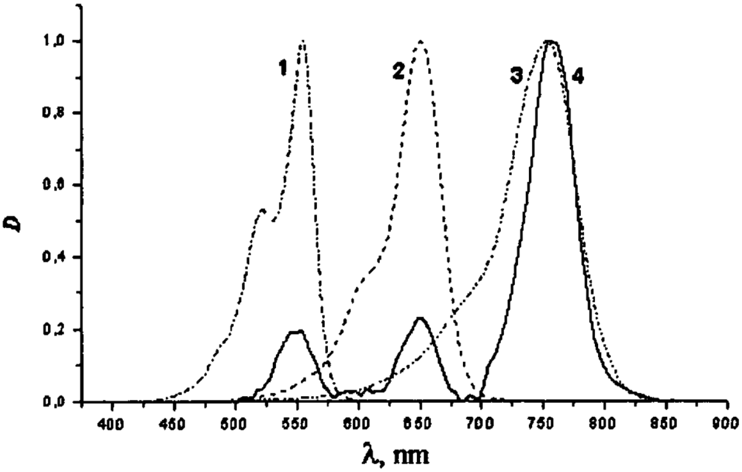


FIGURE 4 Absorption spectra of the dyes **(I)** – 1, **(II)** – 2, **(III)** – 3 and normalized (750 nm) spectrum of the PMMA solution – 4, obtained by MMA radical polymerization in presence of AIBN and the dye **(III)** (chloroform).

inspite of change of corner of inclination of kinetic curves, and speeds of polymerization accordingly, maximal conversion to the monomer for curves 1,3 and 2,4 are identical even regardless the choice of solvent, dye **(I)** serves as the additional initiator of process of polymerization of MMA.

Average molecular mass of polymers which appeared, was determined using viskosimerty (VPJ-1 mark) data at (25 ± 0,1°C) in chloroform solutions. The corresponding values of molecular masses ($K = 0.48$, and $\alpha = 0.8$) are graphically resulted in the Table 1. The values of molecular masses of PMMA confirm, the idea, that dye **(I)** in small concentrations is the initiator of radical polymerization. Dye **(II)** in small concentrations has no influence on the process of polymerization of MMA in selected terms, but at high concentrations it is the initiator of polymerization with low efficiency of initiating. Dye **(III)** in small concentrations has no influence on the process of polymerization of MMA, and in greater concentrations is an inhibitor of the process of radical thermoinitiated polymerization of MMA. The difference between the values of final PMMA molecular masses and the standard experiment without the dye allows us to exclude the ionic reaction mechanism, as the masses would differ very significantly.

The absorption spectrums of solutions of dyes and PMMA in a chloroform were taken off on the Shimadzu UV-3100 spectrophotometer at 293 K in the range of lengths of waves of 350–850 nm. On

Figure 1 the absorption spectrums of solutions of dyes **(I)–(III)** are resulted in a chloroform and PMMA, that appeared during polymerization of MMA in presence AIBN and dye **(III)**.

It is evident from the figure, that in the spectrum of PMMA, which appeared when AIBN and dye **(III)** were used, as well as during conducting of polymerization in mass [7], there are bars of absorption of dye **(III)** and dyes **(I)** and **(II)**, which probably appeared at the radical dissociation of dye **(III)**. Molar correlation of the **(I)** and **(II)** in a polymer is 0,4:0,3:1.

EXPERIMENTAL

Method of Dilatometric Research of Kinetics of Thermo Initiated Homopolymerization

Volume of about 7 ml solution of 1.403 mol/l MMA in DMF, that contains 1% AIBN ($8.43 \cdot 10^{-3}$ mol/l) by mass and dye **(I)–(III)** ($2 \cdot 10^{-4} - 1.3 \cdot 10^{-2}$ mol/l) by a long thin watering-can was carried in dilatometer. The maintenance of dilatometer was vacuumated, and then filled with argon. A process was repeated three times. Dilatometer was placed in thermostatic shirt (80 ± 0,1°C). Prescision is within 0,001. Estimations were carried out with an interval of 1–5 minutes (depending on the size of contractions). After the last estimation the maintence of the dilatometer was carried into a vessel with solidifier. A polymer was filtered and dried to permanent mass. The yield of polymer in 3 experiments without addition of dye was normalized, the calculation of conversion is conducted, calibrating kinetic curve was built.

Kinetic curves in the experiments with dyes were traced using calibration curve with no mass determination of the polimer obtained. Using kinetic curves, the speed of polymerization (Vg) was determined, as a tangent of corner of inclination of curve conversion – time on a stationary area, resulted speed of polymerization of Vg and total constant of speed of polymerization of K_Σ. The order of reaction by an initiator was considered 0, 5, and by a monomer it is 1.

Determination of Average Viscosimetric Molecular Mass of PMMA

Polymers which appeared in each experiment were purified by triple solidification from ethylacetate into isopropanol. The polymers dried up in a vacuum were used for determination of their molecular mass and survey of spectrums of absorption. Viskosimeter was placed in a thermostatic shirt (25 ± 0,1°C). In viskosimeter 7 ml chloroform were placed. After 10–15 min of thermostatification, time of outflowing of chloroform (t0) and preliminary prepared solutions of polymer 4 of known concentrations (t) was measured. The values of characteristic viscosity was determined on wasp of ordinates, which was chopped of a segment on direct dependence of η/C from the concentration of solution of polymer of C (g/100 ml). Taking into consideration, that specific viscidity (η) was numeral evened $\tau/\tau_0 - 1$, molecular mass of PMMA was calculated by a formula: $\lg M = \lg[\eta] - \lg K/\alpha$.

Absorption Spectra

The absorption spectra of dyes solutions and dyed PMMA were taken off in a chloroform on the spectrophotometer of Shimadzu; UV-3100 at 293 K in quartz cuvettes 1 cm thick in the range of lengths of waves of 350–850 nm.

CONCLUSIONS

It is shown that polymerization of MMA in DMF solution in presence of AIBN and polymethine dyes **(I)–(III)** at 80°C, proceeds depending on a chemical structure and concentration of dye. Dye with a short polymethine chain **(I)** in low and middle concentrations initiate the process of polymerization of MMA in solution, in high concentrations dye **(I)** retards a process. As polymethyl chain becomes longer, ability for initiation decreases. Thereby heptamethylcyanin serves as inhibitor of the polymereisation process.

REFERENCES

[1] Bezrodnyi, V. I. & Ishchenko A. A. (2000). *Quantum Electronic*, *12*, 1043–1048.

[2] Bezrodnyi, V. I. & Ishchenko A. A. (2001). *Appl. Phys. B.*, *73*, 283–285.

[3] Bezrodnyi, V. I. & Ishchenko A. A. (2002). *Optics and Laser Technology*, *34*, 1–13.

[4] Ishchenko A. A. (2004). *Quantum Electronics*, *6*, 513–534.

[5] Davidenko, N. A., Ishchenko A. A., & Kuvshynskiy, N. G. (2005). *Fotonika molekulyarnyh poluprovodnikovyh kompozitov na osnovee organicheskih krasiteley*, Naukova dumka: Kiev.

[6] Ishchenko, A. A. (1991). *Stroenie i spektralyno-lyuminiscentnye svoystva polymetinovyh krasiteley*, Naukova dumka: Kiev.

[7] Muravyeva, T. M., Ishchenko, A. A., Horohova, I. E., Dereyanko, N. A., & Dyachkov, A. I. (1991). *Jour. Ppolimernoy Khimii*, *12*, 2520–2524.

[8] Dyumaev, K. M., Manenkov, A. A., Maslykov, A. P., Matyushin, G. N., Nechytaylo, V. S., & Prohorov, A. M. (1991). *Vzaemodeystvie lasernoho izlucheniya s opticheskimi polimerami*, Nauka: Moscow.

[9] Svetlichyi, V. A., Kopylova, T. N., Mayer, G. V., Lapin, I. N., Derevyanko, N. A., & Ishchenko, A. A. (2007). *Quantum Electronics*, *37*, 118–123.

[10] Komarov, I. V., Turov, A. V., Kornilov, M. Yu., Dereyanko, N. A., Ishchenko, A. A. (1989). *Jour. Obschey Khimii*, *59*, 2356–2361.