ISSN 0027-1314, Moscow University Chemistry Bulletin, 2007, Vol. 62, No. 6, pp. 335–342. © Allerton Press, Inc., 2007.
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Radical Polymerization as an Indicator Reaction for Determination of Organic Compounds

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Received March 15, 2007

Abstract—Polymerization of methyl methacrylate (MMA) and 4-vinylpyridine (VP) has been carried out in an aqueous solution in the presence of the initiating system persulfate–tetramethylethylenediamine. The reaction rate has been monitored by measuring the light absorbance of the suspension of the resulting polymer. The effect of 26 model organic compounds on the polymerization rate has been studied. It has been shown that the VP polymerization is inhibited by a smaller number compounds (9 compounds) than the MMA polymerization (22 compounds), which indicates that the former reaction has better selectivity, whereas the determination of model compounds using the MMA polymerization reaction is more sensitive. This is explained by the lower chain growth rate constant for VP vs. MMA and different stationary concentrations of radicals in the systems. The use of these indicator polymerization reactions makes it possible to distinguish some closely related compounds, e.g., 1,4-benzoquinone and 9,10-anthraquinone (MMA reaction) or dinitrophenol and 4-nitrophenol or phenol (VP reaction). Determination of ascorbic acid in a pharmaceutical formulation has been carried out.

DOI: 10.3103/S0027131407060089

Determination of organic compounds by kinetic methods can be based either on their direct effect on the rate of an indicator reaction or on their action on the catalyst (metal ion). The direct effect of organic compounds on the reaction rate is observed, for example, in oxidation of arylamines by hydrogen peroxide (catalysts are derivatives of phosphonic, sulfonic, and carboxylic acids [1]), in the iodine-azide reaction (catalysts are thiols and thiones [2]), and in other systems [3, 4]. On the whole, notwithstanding a large number of separate examples, the determination of organic compounds on the basis of their direct effect on reaction rates remains little studied. In particular, interesting results could be obtained by studying radical chain processes as indicator reactions, since even small concentrations of analytes can exhibit strong effects upon their interaction with chain-carrying radicals present in very low concentrations. For example, chain autooxidation of aryldiamines makes it possible to selectively determine some compounds with high sensitivity [5]. In this context, we considered typical radical reactions, such as radical polymerization reactions.

Polymerization reactions of different monomers in an aqueous solution have been studied [6–8]; however, they have not been used for analytical purposes. Compounds encountered as impurities in monomers or inhibitors added to monomers to stabilize them in storage are known to influence the polymerization rate [8–12]. For the MMA polymerization, the strongest inhibitors are phenols and naphthols, whereas quinones, aromatic amines, and thiols are weaker inhibitors [8]. As a rule, inhibition is chain transfer to the inhibitor to form a radical that is less reactive than radicals ensuring chain propagation. This mechanism is typical of aromatic amines and phenols, which form $ArNH^{\bullet}$ and $ArO^{\bullet}$ radicals [10, 13]. Each of the semiquinone (or arylamine) radicals disproportionates to quinone (quinoneimine) and initial phenol (arylamine) and can terminate one more chain. Polycyclic aromatic compounds, e.g., anthracene, are efficient inhibitors of polymerization of vinyl monomers [13, 14], which is explained by their ability to be excited to the biradical state due to their polyconjugated structure. Inhibition by quinones [9, 12, 13] and other unsaturated compounds occurs through their addition to double bonds to yield less reactive products as compared to the initial radicals. The most active inhibitor among quinones is *p*-benzoquinone [9]. Nitroaromatic compounds are even more active inhibitors. Their action is based on the formation of a stable radical, nitrogen monoxide [9]. Nitroso compounds have an analogous action [15].

Chain-transfer reagents (e.g., alkylamines) have no considerable inhibiting effect on polymerization since the nascent amine radicals are rather active [12, 13]. Acetic acid, acetaldehyde, acetone, methanol, benzene, and toluene were also found to be chain-transfer reagents; however, the polymerization rate did not change in their presence (presumably, for the same reason) [16]. In most cases, oxygen acts as an inhibitor, which is attached to the chain and forms peroxy radicals [16].

In this work, we studied the possibility of using radical polymerization reactions as indicator reactions in kinetic methods of analysis. To do this, we needed to

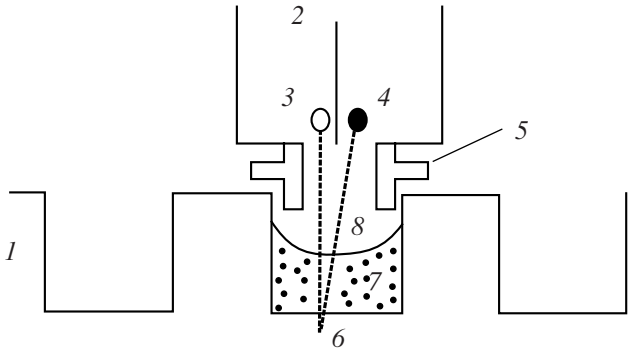

Fig. 1. Scheme of the measurement of the optical density of a polymer suspension with the use of a reflectometer: (*1*) 96-hole plate, (*2*) reflectometer probe, (*3*) LED, (*4*) photodiode, (*5*) aluminum orifice, (*6*) white support, (*7*) polymer suspension, and (*8*) light flux

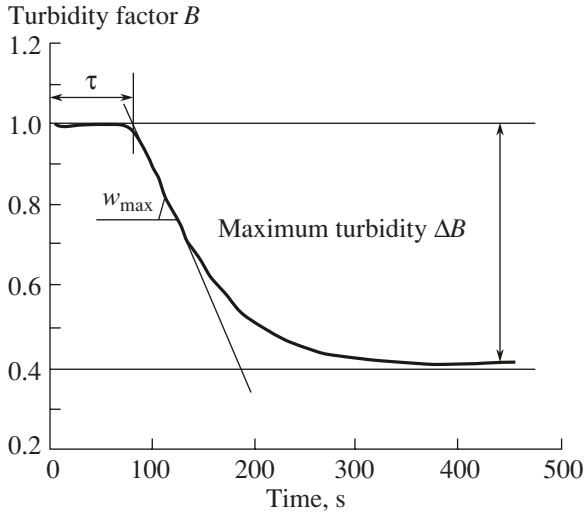

Fig. 2. Typical dependence of the turbidity factor B of a polymer suspension on time for the MMA or VP polymerization reaction in solution and the ΔB and τ parameters used for characterizing these reactions.

carry out the polymerization of selected monomers (methyl methacrylate and 4-vinylpyridine) in an aqueous solution, find a simple method for monitoring the reaction rate, and study the effect of model compounds on the polymerization rate.

EXPERIMENTAL

Reagents, Solutions, and Instrumentation

Reagent grade or analytical grade reagents were used. Distilled water purified with a Millopore system (resistivity, 18 MΩ cm) or ethanol (Bryntsalov-A, Russia) were used for preparing solutions. Methyl methacrylate (MMA) and 4-vinylpyridine (VP) (Merck) were vacuum distilled and stored only at 5°C. *N*,*N*,*N*',*N*'-Tetramethylethylenediamine (TEMED) (Helicon, Russia) was used as purchased. $K_2S_2O_8$ (Reakhim, Russia) was recrystallized from water. Aqueous solutions of $K_2S_2O_8$ (0.1 mol/L), VP (0.3 mol/L), and MMA (0.1 mol/L) were kept for 24 h before use, stored at 4°C, and used within 5 days. An acetate buffer solution (pH 3.8–6.5) was prepared from 0.02 M CH_3COONa and 0.02 M CH_3COOH, and a borate buffer solution (pH 8.0) was prepared from 0.05 M $Na_2B_4O_7 \cdot 10H_2O$ and 0.1 M HCl. Ascorbic acid (Sigma-Aldrich) was dissolved in water purged with nitrogen, and the solutions were used on the day they were prepared.

Turbidimetric measurements were taken with a Uniphot-test-405 portable reflectometer (Marafon, Russia) [17] in a 96-well polystyrene plate. The light from a red light-emitting diode (LED) passed through the solution in a well in which a polymer suspension formed, reflected from a white paper sheet placed under the plate, passed again through the suspension, and recorded by a photodiode (Fig. 1). A red LED (650 nm) was used since it ensured the highest intensity among available LEDs and the light absorbance of a suspension was slightly dependent on the wavelength.

Reaction Procedure and Data Processing

Polymerization was carried out at room temperature (23 ± 1°C). Reagents were mixed in a well of the plate in the following order: an acetate buffer solution (pH 6.5, 15 μL), monomer (VP, 0.3 mol/L, 75 μL, or MMA, 0.09 mol/L), initiator (TEMED, 0.9 or 0.01 mol/L, 15 μL), and a model compound or pure water; then, the solution was stirred with a pipette tip, and a potassium persulfate solution (0.1 mol/L, 15 μL) was added. The mixture was stirred for 3 s, and measurements were begun. The photodiode voltage U, recorded every second (an RS-232 interface), decreased with an increase in the turbidity of the solution. The turbidity factor B was calculated by the formula

$$B = \frac{U - U_{black}}{U_{white} - U_{black}},$$

where U_{black} is the voltage on the LED placed in a closed dark box, and U_{white} is the voltage obtained from an absolutely transparent aqueous solution in a well of the plate. Thus, $U_{white} - U_{black}$ is the maximal range of the U value. Correspondingly, the B value was unity at the beginning of the run and decreased as polymerization proceeded (Fig. 2).

RESULTS

Choice of Monomers, Initiator, and Analytical Signal

The polymerization reaction used as the indicator one should proceed in an aqueous solution at room temperature. To select a suitable reaction, reactions were carried out in a neutral medium (an acetate buffer solution pH 6.5). Three monomers with a rather high solubility in water were studied: methacrylamide, MMA,

Table 1. Effect of the persulfate concentration on the polymerization reaction parameters[a] ($n = 3$, $P = 0.95$)

Monomer	VP[b]			MMA[c]		
C ($K_2S_2O_8$), mol/L	0.01	0.03	0.10	0.01	0.03	0.10
Induction period[d] τ, s	150	120	51	180	130	70
Maximum turbidity[e] ΔB	0.45	0.48	0.54	0.63	0.65	0.68

Notes: [a] All concentrations refer to of initial solutions; [b] 0.3 mol/L of VP, 0.9 mol/L of TEMED; [c] 0.09 mol/L of MMA, 0.01 mol/L of TEMED; [d] the reproducibility of τ was ±8–10 s for τ > 100 s and ±5 s for τ < 100 s; [e] the reproducibility of ΔB was ±0.05.

Table 2. Effect of the TEMED concentration on the polymerization reaction parameters (concentration of $K_2S_2O_8$, 0.1 mol/L; $n = 3$, $P = 0.95$)

Monomer	VP					MMA		
C^a_{TEMED}, mol/L	0.04	0.2	0.6	0.9	1.3	0.01	0.10	1.0
Induction period[b] τ, s	65	58	53	51	36	70	45	0
Maximum turbidity[c] ΔB	0.05	0.15	0.49	0.54	0.33	0.68	0.64	0.58

Notes: [a] The concentration in the added solution; [b] the reproducibility of τ was ±5 s; [c] the reproducibility of ΔB was ±0.03 (at $\Delta B < 0.3$) and ±0.05 (at $\Delta B > 0.3$).

and VP. We found that the last two monomers polymerize in an aqueous solution (the initiating system will be discussed later) to form turbid suspensions that do not precipitate for several minutes. The introduction of ethanol (≥0.5%) into the reaction mixture prevents the formation of a suspension. This is most likely associated with chain termination rather than with an increase in the solubility of the nascent polymer. The inhibiting effect of water-miscible organic solvents was previously observed in polymerization of acrylamide [6].

Figure 2 shows the resulting kinetic curve. The turbidity caused by formation of an insoluble polymer is observed with a delay of a few minutes. Such a delay can be caused by different factors: accumulation of some minimal concentration of a polymer necessary for its coagulation; the presence of dissolved oxygen, which rapidly reacts with active radicals, thus inhibiting the process; or chain termination or transfer (in the presence of model compounds). Hereinafter, the observed turbidity delay is referred to as induction period.

Thus, the reaction was characterized by two parameters: the maximum turbidity ΔB related to the amount of the formed polymer (the difference between the turbidity factors prior to the reaction and after its completion at $t = 400$ s) and the induction period τ. The maximal reaction rate w_{max}, determined as the slope of the kinetic curve at the point of its inflection, turned out to be less reproducible.

For initiation of polymerization, we studied the water-soluble initiator 2,2'-azobis(isobutyrate), which decomposes into radicals; however, in its presence, polymerization of VP and MMA did not begin even at 60°C. We also studied redox initiating systems [6, 9] containing persulfate, bromate, periodate, or hydrogen peroxide (including $H_2O_2 + Fe^{II}$) as the oxidant and thiosulfate, hydrazine, dimethylamine, diethylamine, triethylamine, or TEMED as the reductant. Polymerization occurred only in the presence of persulfate (0.1 mol/L) as the oxidant and thiosulfate, hydrazine, or TEMED (0.01 mol/L) as the reductant. It is likely that, in these systems, the highest concentration of free radicals is achieved. The strongest turbidity of MMA and VP solutions is observed in the persulfate–TEMED system; polymerization had the induction period (~1 min). This initiating system is often used for polymerization of acrylamide in preparation of gels for protein separation [18]. The use of hydrazine or thiosulfate as the reductant of the initiating system leads to lower maximal ΔB values and a longer induction period (3–13 min). Subsequently, the persulfate–TEMED initiating system was used for studying VP and MMA polymerization.

Effect of Reactant Concentrations and pH

To achieve considerable conversions after only a few minutes, highly concentrated aqueous solutions of a monomer are required (a near-saturated solution of MMA (0.09 mol/L) or VP (0.3 mol/L). With an increase in the $K_2S_2O_8$ concentration, the induction period decreases while the depth of reaction increases (Table 1). High TEMED concentrations lead to a decrease in ΔB upon VP polymerization (Table 2), which can be due to a too high initiation rate and formation of shorter polymer chains or to a too rapid decomposition of persulfate upon its interaction with an excess of TEMED. It is desirable that the ΔB value be maximal and the induction period be shorter than 1 min; therefore, we used a 0.9 M (for VP) or 0.01 M (for MMA) TEMED solution in the presence of a 0.1 M persulfate solution.

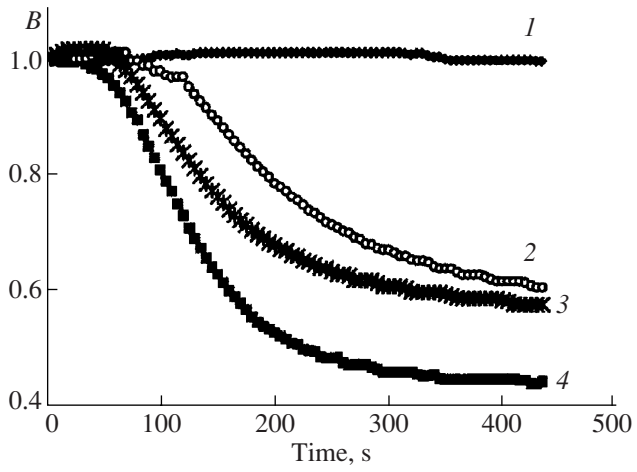

Fig. 3. Kinetic curves of the VP polymerization reaction in the presence of different concentrations of 2,4-dinitrophenol:(*1*) 0.01, (*2*) 1×10^{-3}, (*3*) 1×10^{-5}, and (*4*) 0 mol/L.

Solution acidity in the range of pH 3.9–8.0 has no noticeable effect on the polymerization rate (for example, during VP polymerization, ΔB was in the range 0.51–0.55). All further experiments were carried out in neutral medium (pH 6.5, an acetate buffer solution). Throughout this work, the volumes of solutions used for polymerization (see Experimental) were the same.

Effect of Model Organic Compounds

Model compounds were selected among compounds known to affect the polymerization rate—phenols, amines, nitrosamines, and sulfur(2–) compounds [9–13]—and among compounds with indifferent functional groups (carboxyl, amide). The maximal initial concentration of model compounds was 0.01 mol/L (in some cases, 0.1 mol/L). The compounds under consideration either have no effect on the reaction rate or retard the reaction. The kinetic curves in Fig. 3 show that an increase in the concentration of a model compound decreases the depth of reaction ΔB and the maximal reaction rate w_{max}; the induction period τ can thereby increase. Figures 4 and 5 show the plots of ΔB and τ versus the concentration of a compound. A compound was considered to influence the reaction rate if a parameter (ΔB or τ) fell beyond the confidence interval for the blank (delimited by dashed lines in Figs. 4 and 5). In particular, phenol, 2,4,6-trinitrophenol, and 2,4-dinitrophenol have an effect on the depth of polymerization of VP beginning with the concentration 0.01, 1×10^{-3}, and 1×10^{-5} mol/L, respectively.

The results of studying the effects of model compounds on the progress of both reactions are summarized in Table 3. Only the following compounds inhibit the VP polymerization reaction: methyl- and ethylamines, cysteine and thiosalicylic acid anions, *p*-benzoquinone, and some phenols. At the same time, nearly all selected compounds inhibit the MMA polymerization reaction, and the minimal detectable concentrations are, as a rule, lower in this case. Hydroquinone, *p*-benzoquinone, 2,4-dinitrophenol, and ascorbic acid have the strongest effect.

Model compounds differently affect the kinetic curve parameters ΔB and τ. For the VP polymerization, only phenol, hydroquinone, *p*-benzoquinone, and picric acid change the induction period of the reaction, whereas the maximum turbidity is affected not only by the above compounds but also by two amines and two SH compounds. For the MMA polymerization, the

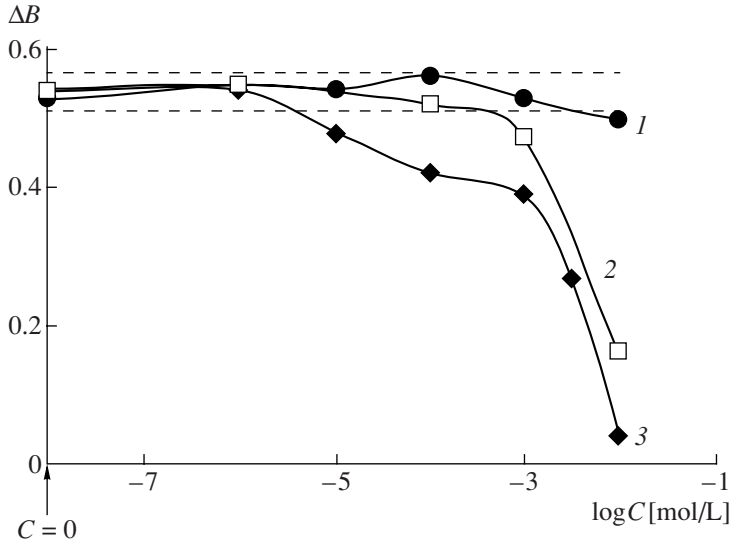

Fig. 4. Effect of phenols on the depth of the VP polymerization reaction: (*1*) phenol, (*2*) 2,4,6-trinitrophenol, and (*3*) 2,4-dinitrophenol. Dashed lines delimit the confidence interval of the blank; the point with $C = 0$ corresponds to the ΔB value in the absence of model compounds.

opposite situation was observed: the minimal detectable concentrations calculated from τ were the same or even lower (for nine model compounds) than those calculated from ΔB.

It is worth noting that analytical signals are different within similar groups of compounds. For example, the VP polymerization reaction is retarded only by methyl- and ethylamines and not by other amines (secondary and ternary, *n*-propylamine, and aniline, which have no detectable effect up to the concentration 0.01 mol/L). In the MMA polymerization reaction, primary C_1 and C_2 amines also have a stronger effect than the other amines (the minimal detectable concentrations differ by two to three orders of magnitude). In the VP polymerization reaction, different phenols have a very different effect (Fig. 4), which makes it possible to detect 2,4-dinitrophenol or 2,4,6-trinitrophenol in the presence of 4-nitrophenol or phenol. These phenols in concentrations 1×10^{-3} mol/L do not interfere with the determination of 3×10^{-3} M 2,4-dinitrophenol. The difference in the effect of quinones was observed in the MMA polymerization reaction (Fig. 5); for example, *p*-benzoquinone in concentrations 1×10^{-7}–1×10^{-4} mol/L inhibits the polymerization, whereas 9,10-anthraquinone has no effect on it.

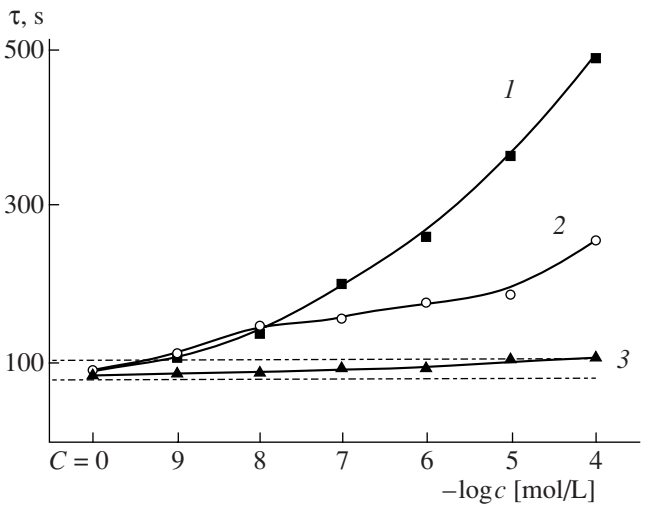

Fig. 5. Effect of (*1*) hydroquinone, (*2*) 1,4-benzoquinone, and (*3*) 9,10-anthraquinone on the induction period of the MMA polymerization reaction. Dashed lines delimit the confidence interval of the blank.

Determination of Ascorbic Acid in a Medical Product

The determination of a model compound by the MMA polymerization reaction is more sensitive than by the VP polymerization reaction (Table 3). The question arises of whether the former reaction allows one to determine compounds with the selectivity required for analysis of actual objects. The determination of ascorbic acid (HAsc) was carried out in freshly unsealed ampoules of Bravinton (sol. inj.) (Table 4). The analyte solution was introduced into the MMA polymerization reaction instead of a model compound. The detection limit of ascorbic acid in an aqueous solution was 10^{-7} mol/L, which is close to its detection limit by chemiluminescence and some spectrophotometric methods [22]. The plot of ΔB versus the HAsc concentration in water covers the range 1×10^{-3}–1×10^{2} mol/L, which corresponds to the HAsc concentration in the drug. However, the introduction of an aliquot of the undiluted drug into the reaction led to overestimated results: $(3.5 \pm 0.2) \times 10^{-3}$ instead of 3.1×10^{-3} mol/L; therefore, we checked the effect of the other components of the drug. Sodium metabisulfite interfered with the determination, whereas the other components, separately or in combination with HAsc, had no effect on the reaction rate. For lower concentrations than those in the drug but at the same ratio of the HAsc and $Na_2S_2O_5$ concentrations, metabisulfite did not interfere with the determination of ascorbic acid; therefore, for analysis, the drug solution was diluted tenfold to obtain HAsc and $Na_2S_2O_5$ concentrations on the order of 3×10^{-3} and 7.5×10^{-3} mol/L, respectively. The calibration plot of ΔB versus HAsc concentration covers the range 1×10^{4}–1×10^{-3} mol/L ($r = 0.992$, $s_r = 0.08$ for 3×10^{-3} mol/L, $n = 3$). The concentration of HAsc in Bravinton determined from this plot, $(3.2 \pm 0.2) \times 10^{-3}$ M, corresponded to the actual content 3.1×10^{-3} mol/L, which was also confirmed by liquid chromatography with a UV detector, $(3.1 \pm 0.1) \times 10^{-3}$ mol/L ($n = 3$, $P = 0.95$).

DISCUSSION

Major interest in the reactions under consideration as indicator reactions is due to the possibility of selective determination of compounds with similar structures. To interpret our results, we need to consider the scheme of the polymerization process and the role of model compounds in it.

Effect of Chain-Terminating Compounds

The polymerization of VP and MMA, like of other monomers, involves the stages of chain initiation, propagation, and termination (Table 5). A model compound InH can react with the radical of the initiator R$^\bullet$ or with the radical of the growing chain chain$^\bullet_n$ (reactions (7) and (8)). If the radical of a model compound In$^\bullet$ has low reactivity, both reactions will lead to chain termination. This is likely responsible for the inhibition of polymerization by most model compounds (Table 3). In the case of unsaturated compounds, the inactive radical In$^\bullet$ can also form as a result of addition of the chain-propagating radical to the double bond. This is possible for ascorbic acid, one of the strongest inhibitors of the MMA polymerization (a longer induction period was observed only for hydroquinone, a classical inhibitor of monomers). Ascorbic acid also decreases the polymerization rate. This compels us to assume that the product

Table 3. Effect on model compounds on VP and MMA polymerization. Minimal detectable concentrations (mol/L) that change the induction period τ and the maximum turbidity Δ*B* (these two values are separated by a slash) are given. "No effect" means that there is no difference from the blank at the highest concentration studied (0.01 mol/L)

Compound	Minimal detectable concentration of a compound in the polymerization reaction of	
	VP by τ/Δ*B*	MMA by τ/Δ*B*
Amines and other nitrogen-containing compounds		
Methylamine	No effect/1×10^{-4}	$1 \times 10^{-6}/1 \times 10^{-5}$
Dimethylamine	No effect	$1 \times 10^{-4}/1 \times 10^{-3}$
Trimethylamine	No effect	$1 \times 10^{-3}/1 \times 10^{-3}$
Ethylamine	No effect/1×10^{-3}	$1 \times 10^{-6}/1 \times 10^{-5}$
Diethylamine	No effect	$1 \times 10^{-3}/1 \times 10^{-3}$
Triethylamine	No effect	–
n-Propylamine	No effect	$1 \times 10^{-5}/1 \times 10^{-5}$
Aniline	No effect	$1 \times 10^{-5}/1 \times 10^{-4}$
Glycine	No effect	0.01/No effect
Hydrazine	No effect	0.01/0.01
N-nitrosodimethylamine	No effect	$1 \times 10^{-6}/1 \times 10^{-4}$
Urea	No effect	0.01/0.01
Sulfur-containing compounds		
Thiosulfate	No effect	0.01/0.01
Thiourea	No effect	$1 \times 10^{-4}/1 \times 10^{-4}$
Thiosalicylic acid	No effect/1×10^{-4}	–
Cysteine	No effect/1×10^{-3}	–
Phenols and Quinones		
Phenol	1×10^{-4}/No effect	$1 \times 10^{-6}/1 \times 10^{-5}$
Hydroquinone	$1 \times 10^{-3}/1 \times 10^{-4}$	$1 \times 10^{-8}/1 \times 10^{-8}$
p-Benzoquinone	$1 \times 10^{-3}/1 \times 10^{-3}$	$1 \times 10^{-8}/1 \times 10^{-8}$
9,10-Anthraquinone	–	$1 \times 10^{-5}/1 \times 10^{-4}$
p-Nitrophenol	No effect	$1 \times 10^{-5}/1 \times 10^{-5}$
2,4-Dinitrophenol	No effect/1×10^{-4}	$1 \times 10^{-7}/1 \times 10^{-7}$
2,4,6-Trinitrophenol	$0.01/1 \times 10^{-3}$	$1 \times 10^{-5}/1 \times 10^{-5}$
Other compounds		
Ascorbic acid	No effect	$1 \times 10^{-7}/1 \times 10^{-6}$
Benzoic acid	No effect	No effect
Salicylic acid	No effect	$1 \times 10^{-4}/1 \times 10^{-3}$

of its transformation is also an inhibitor, even if a weaker one than the acid itself. For quinones, the mechanism of inhibition due to addition to double bonds cannot be ruled out as well.

Effect of Chain-Transfer Agents

If the radical In$^{\bullet}$ forming in reactions (7) and (8) is sufficiently active to initiate a new chain, the result will be chain transfer, which leads to a decrease in the physical length of polymer chains and an increase in their number. This is likely responsible for the effect of methyl- and ethylamines on the polymerization rate (Table 3, Fig. 5). Such an effect is unexpected since primary amines are neither among typical inhibitors of bulk polymerization nor among typical radical scavengers (alkylamine radicals are considerably less stable than radicals formed from compounds of other classes). If chain is transferred to amine, the nascent radical can rather rapidly initiate the growth of a new chain; i.e., the overall rate of the process will not change. However, the effect of amine will manifest itself not only in bulk polymerization; under our conditions, a decrease in chain length can lead to a decrease in the turbidity of the suspension.

Difference in the Properties of Monomers

To elucidate the difference in the characteristics of the indicator reactions involving VP and MMA (Table 3), we should reveal the difference in properties between the monomers since the initiating system is the same in all cases. As is known, the reactivity of vinyl monomers noticeably depends on the resonance stabilization energy [19, p. 25]: monomers with a higher degree of conjugation are more reactive but their radicals are less active, whereas less conjugated monomers are less reactive but form very active radicals. Conjugation in the VP molecule should be considerably more pronounced than in the MMA molecule; therefore, VP radicals are expected to be less reactive. Indeed, the reaction rate constants at 25°C are 2.7×10^2 and 12 L/mol s for MMA and VP, respectively [20, 21]. The polymerization rate w is related to the chain propagation rate constant k_p, the stationary radical concentration [R$^{\bullet}$], and the monomer concentration [M] as follows [10, p. 14]:

$$w = k_p[R^{\bullet}][M], \quad (9)$$

For the quadratic chain termination,

$$[R^{\bullet}] = (w_{in}/k_0)^{1/2},$$

where w_{in} is the initiation rate, and k_0 is the termination rate constant. Based on the maximum turbidities, determined gravimetrically, and measurements of the light absorbance of the polymer suspension, we estimated the observed polymerization rate constants k_{obs}, which are equal to $k_p[R^{\bullet}]$ according to Eq. (9). For MMA and VP, these values are close: $(1.2 \pm 0.1) \times 10^3$ and $(1.0 \pm 0.2) \times 10^3$ s^{-1}, respectively ($n = 3$, $P = 0.95$). If the k_{obs} constants of two monomers are close to each other and the k_p constants differ more than 20-fold, the [R$^{\bullet}$] values should also be different; namely, stationary concentra-

Table 4. Composition of Bravinton solution for injections (g/L)

Ascorbic acid	Vinpocetine[a]	Tartaric acid	Sodium metasulfite	Sorbitol	Benzyl alcohol
0.55[b]	5.0	10	0.23	10	10

Notes: [a] Another name for Cavinton, a semisynthetic alkaloid; [b] 3.1×10^{-3} mol/L.

Table 5. Basic stages of the polymerization reaction used in this work

In th absence of model compounds (mon = VP or MMA):	
Redox initiation: TEMED + $S_2O_8^{2-} \longrightarrow R^\bullet$ ($R^\bullet = SO_4^{\bullet-}$, TEMED$^\bullet$, etc.)	(1)
(presumably the rate-limiting stage [15])	
Interaction of radicals of the initiating system with the monomer:	
$R^\bullet$ + mon $\longrightarrow$ mon$^\bullet$	(2)
Chain propagation: mon$^\bullet$ + mon $\longrightarrow$ $(\text{mon})_2^\bullet$	(3)
$\text{chain}_n^\bullet$ + mon $\longrightarrow$ $\text{chain}_{n+1}^\bullet$ (growing radical containing $n + 1$ monomer units)	(4)
Chain transfer to the monomer:	
$\text{chain}_n^\bullet$ + mon $\longrightarrow$ chain_n + mon$^\bullet$ (limiting the length of chain_n)	(5)
Termination: $R^\bullet \longrightarrow$, mon$^\bullet \longrightarrow$, $\text{chain}_n^\bullet \longrightarrow$ } radical loss (e.g., by the reaction with another radical)	(6)
Additional stages in the presence of model compounds (InH)	
Radical exchange $R^\bullet$ + InH $\longrightarrow$ In$^\bullet$ + RH	(7)
Chain transfer to a model compound: $\text{chain}_n^\bullet$ + InH $\longrightarrow$ In$^\bullet$ + chain_n	(8)

tions of radicals in a mixture upon VP polymerization should be higher than upon MMA polymerization.

The above interpretation of the difference between the systems under consideration is schematic and tentative; however, it allows us to explain the different effect of model compounds in these two reactions. At low radical concentrations (i.e., in the case of MMA), a considerable fraction of radicals can be trapped by almost any model compound; most of these compounds will decrease the overall polymerization rate. At higher radical concentrations (in the case of VP), higher concentrations of rather active inhibitors are required to achieve the same effect. This is actually the case (Table 3): the MMA polymerization rate is affected by 22 model compounds, whereas the VP polymerization rate responds to the presence of only nine model compounds and the minimal concentrations of these compounds that affect the reaction rate are always lower than in the case of MMA.

If we assume that a model compound reacts not only with the most active radicals of the initiating system but also with the radicals of the monomers or growing chain, it should be taken into account that lower reactivity of radicals with a higher degree of conjugation (VP) makes them more selective, i.e., less sensitive to side reactions [19], in particular, to chain transfer to a model compound (Table 5, Eq. (8)). This means that the probability of MMA reacting with a model compound is higher than that of VP.

Applying the aforesaid to the effect of, for example, alkylamines, we may assume that higher concentrations of methyl- or ethylamine are necessary to affect the chain propagation rate during polymerization of VP than of MMA. Indeed, the polymerization of MMA is more sensitive to the presence of amine (Table 3).

Effect on the Induction Period and Maximum Turbidity

The different character of the effect of model compounds on the induction period and the maximum turbidity can be considered from the standpoint of the reaction of a monomer. As follows from Table 3, for some compounds, minimal detectable concentrations are different depending on what parameter was measured (τ or ΔB). In addition, the determination based on the VP polymerization reaction is more sensitive when ΔB is measured (for example, 1×10^{-4} mol/L of hydroquinone changes the maximum turbidity, whereas 1×10^{-3} mol/L is required to affect the induction period; the same is observed for the other compounds except phenol). Conversely, the determination based on the MMA polymerization reaction is more sensitive

when the induction period is measured. According to the above assumption, the VP polymerization is characterized by higher concentrations of the radicals of the initiating system ($R^{\bullet}$) and growing chains ($chain_n^{\bullet}$); therefore, the reactions of model compounds (chain transfer and radical exchange, Eqs. (7) and (8), Table 5) will be of more significance in polymerization of VP than in polymerization of MMA.

To verify the suggested scheme of the action of model compounds, it would be of interest to study the polymerization of an unconjugated monomer with an even lower chain propagation rate constant (for example, vinylidene chloride, $k = 8.6$ [20]) with the use of the same initiating system TEMED–persulfate. The range of compounds that have an effect on the rate of this reaction should be as narrow as or even narrower than for VP polymerization, and model compounds should mainly affect the depth of the reaction rather than its induction period. This could be the subject of a separate study.

CONCLUSIONS

Indicator polymerization reactions in an aqueous solution are applicable to the determination of organic compounds acting as radical scavengers, as well as of some compounds that are not typical inhibitors of chain reactions, e.g., alkylamines. Noteworthy is the fact that some compounds with similar structures can be distinguished or one reducing agent can be determined in the presence of another (ascorbic acid/metabisulfite). Inasmuch as many compounds have an inhibiting effect, analysis of specific objects will require studying the effect of the matrix and carrying out calibration on the background of all components that can affect the analytical signal.

Our findings allow us to suggest the principle of further selection of indicator polymerization reactions (with redox initiation). If high sensitivity is required, less active monomers should be chosen, which give active radicals [19, p. 5], e.g., acrylonitrile, vinylidene chloride, or maleic anhydride. If selectivity is of primary importance, more reactive monomers should be used, e.g., isoprene, styrene, or acrylamide [19, p. 5]. To optimize the conditions of polymerization of these monomers in solution will be a separate task.

ACKNOWLEDGMENTS

We are grateful to N.S. Melik-Nubarov for valuable methodological advice and supplying reagents, I.F. Dolmanova for helpful discussions, S.G. Dmitrienko for the sample of 4-vinylpyridine, and A.V. Moiseeva for her help with the experiment.

This work was supported by the Russian Foundation for Basic Research (project no. 04-03-33116).

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