

ANIONIC POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF *p*-BENZOQUINONE

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An investigation was made of the effect of *p*-benzoquinone on anionic polymerization of methyl methacrylate in benzene solution, initiated with sodium tert-butoxide at 20°C; kinetic data were measured by means of the dilatometric method. It was found that if the molar ratio of tert-butoxide to *p*-benzoquinone in the polymerization mixture is ≤ 1 , no polymerization takes place. It is assumed that the reaction of sodium tert-butoxide with *p*-benzoquinone leads to an addition of one molecule of tert-butoxide to one molecule of benzoquinone and to condensation reactions between quinone rings; although the reaction products are not catalytically active with respect to polymerization, they nevertheless are able to activate the excess of tert-butoxide, raise the polymerization rate and affect the stereospecific growth of the chain, thus also influencing the amount of the isotactic component in poly(methyl methacrylate). The tacticity of the polymers was investigated using the NMR method.

p-Benzoquinone is a commonly used monomer stabilizer of the acryl type, and removal of its residues from the monomer before polymerization is labour-consuming. The effect of *p*-benzoquinone on the kinetics of anionic polymerization has been investigated several times¹. For initiation of the polymerization of methyl methacrylate with diethyl cadmium the authors^{1,2} assume that the increase in the polymerization rate is due to the formation of free radicals. Similarly, the paper dealing with the polymerization of styrene initiated with lithium metal is also based on an assumption⁴ of the ion-radical mechanism.

The present paper is devoted to the anionic polymerization of methyl methacrylate with sodium tert-butoxide⁵ in the presence of *p*-benzoquinone with respect to the effect of quinone upon the tacticity of the polymers.

EXPERIMENTAL

Methyl methacrylate (commercial product, Synthesia, Pardubice) was purified and dried as described⁵. Benzene, thiophene free, was purified in the usual way and dried over sodium metal. *p*-Benzoquinone (commercial product, Lachema, Brno) was twice free crystallized from ethyl alcohol and then twice sublimated under normal pressure at 100°C; m.p. 115.0°C. The polymerization was carried out in lens-shaped dilatometers, approx. 40 mm dia., approx. 10 mm high and approx. 10 ml in volume, provided with a magnetic stirrer in a thermostat at $20 \pm 0.01^\circ\text{C}$. All operations involved in the purification of the individual chemicals and equipment and in the dosing of the reaction components into the dilatometers were performed in dry oxygen-free

argon. The dilatometers were dried at 130°C 20 h and then evacuated (10^{-2} Torr) while annealed in flame. The reaction components were dosed by means of syringes with long needles; during dosing, the contents of dilatometers were stirred with the magnetic stirrer. The polymerization was terminated with a methanol solution of hydrochloric acid, the polymers were isolated and purified by double precipitation from a chloroform solution into an excess of methanol and dried at 40°C/ 10^{-2} Torr to constant weight. Viscosity of the chloroform solutions was measured in an Ubbelohde diluting viscometer and the molecular weight was calculated from⁶ $[\eta] = 3.4 \cdot 10^{-5} M^{1.83}$. Tacticity of the polymers was determined by the NMR method with a JNM-3-60 apparatus. The reaction of sodium tert-butoxide (*I*) with *p*-benzoquinone (*II*) was carried out at room temperature in conic ampoules in argon. To a benzene solution of *II*, a benzene solution of *I* was added. The reaction product was centrifuged, and the unreacted alkoxide was determined acidimetrically in the solution over the precipitate.

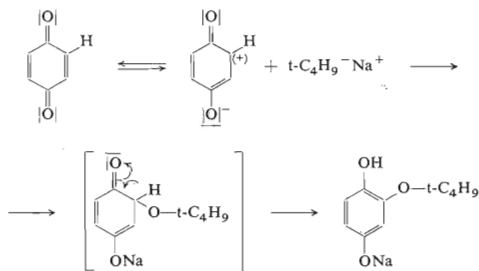
RESULTS AND DISCUSSION

Reaction of Tert-butoxide (I) with p-Benzoquinone (II)

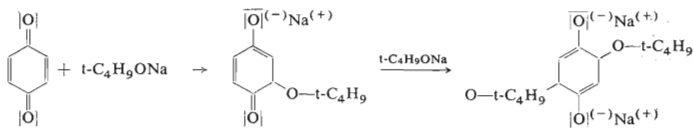
p-Benzoquinone reacts with the alkaline reagents, yielding a number of addition and condensation compounds^{7,8}. Condensation of several quinone rings, accompanied by some reduction-oxidation processes, gives rise to humic acids without any precisely defined structure⁸. Their presence in the reaction mixture is revealed by the deep-green colour of the solution, and also by the formation of an insoluble precipitate of the same colour. Our experimental results confirm that these products have no catalytic activity with respect to polymerization. The addition of *I* to the quinone ring may occur similarly to the case of the Grignard reagents or organolithium compounds⁷. Theoretically, one or two molecules of the agent may be added to one molecule of *II*, at positions 1, 2 or 1, 4. The lithium reagents are added prevailing at position 1, 2; the Grignard reagents may occupy both positions 1, 2 and 1, 4. The probability of the addition 1, 4 is highest for simple and sterically unhindered quinones of the benzene series. The same probability is also assumed for reaction of *I* with *p*-benzoquinone⁹. One or two molecules of *I* could be added to one molecule of *II* (Scheme 1 or 2).

The results obtained by an investigation of the stoichiometric reaction between *I* and *II* (Table I) could be a reason for preferring the two-step addition (Scheme 2). It was found, however, that *a*) the product of addition of *I* to *II* in the ratio $\leq 1 : 1$ is not catalytically active for polymerization (Table II); *b*) polymerization does not occur until the molar ratio *I* : *II* has become larger than 1 : 1 (practically up to 100% conversion, starting at very low concentrations of *I* – 0.05 mol.% related to monomer). Since there is no reason why to assume that the product of the two-step addition would be able to initiate polymerization, while the product of addition of a single molecule would not, it seems likely that the addition occurs to the first step only (Scheme 1). The second molecule of butoxide *I* is apparently not added to quinone *II* and is bonded by mere physical forces. It is, however, activated by the action of the reaction product of the one-step addition, which is reflected in the course and rate of polymerization (Fig. 1). The reaction product between *I* and *II* can affect both the initiation and growth reactions. Moreover, an addition to the second step would probably be very difficult owing to the charge distribution on the aromatic ring of the

reaction product (Scheme 1, 2). The acidity of the hydrogen atom at the second oxygen atom (Scheme 1) is so weak because of the inductive effect of the anion that its reaction with *I* will probably not take place at all; neither will a strong complex be formed. This reaction would probably yield tert-butyl alcohol as its product, which would considerably extend the induction period and reduce the molecular weight of the polymer by transfer¹⁰. The phenoxide anion is strongly conjugated with the aromatic ring in the case of the one-step addition, and is therefore incapable of initiating anionic polymerization.



SCHEME 1



SCHEME 2

Kinetics of Polymerization of Methyl Methacrylate

At a constant concentration of sodium tert-butoxide as a catalyst the rate of polymerization increases with the initial monomer concentration; it is considerably accelerated by the presence of *p*-benzoquinone (Fig. 1). Under the given concentration conditions, the reaction rate compared with respect to the initial monomer concentration is approximately 3.0 for polymerization both with quinone and without it. The effect of the concentration of quinone *II* on the rate of polymerization at constant concentrations of the monomer and the initiator *I* can be seen in Fig. 2. Similarly to papers^{1,11} the curves of dependence of the polymerization rate on the concentration of *II* have a maximum whose position depends on the initial concentration of *I*.

If the initial content of the initiator is higher (0.5 mol.% per monomer), the maximum rate is attained at a quinone concentration 50 mol.% (related to tert-butoxide); the position of the maximum remains unchanged with increasing concentration of I .

TABLE I

Stoichiometry of the Reaction of Sodium Tert-butoxide (I) with p -Benzoquinone (II) in Benzene Solution

Concentration indexes: o starting, s in solution after a reaction lasting 1–2 s, p in precipitate.

I_0	II_0	I_0/II_0	I_s	I_p/II_p
0.140	0.0696	2.01	0.0056	1.9
0.140	0.0336	4.18	0.0824	1.7
0.140	0.0136	10.3	0.1004	2.6
0.014	0.0062	2.1	—	2.1
0.014	0.0066	2.2	—	2.2
0.014	0.0040	3.5	0.0028	2.8
0.052	0.026	2.0	0.015	1.4
0.117	0.029	4.0	0.045	2.4
0.139	0.069	2.0	0.013	1.8

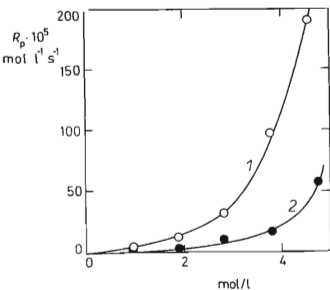


FIG. 1

Dependence of the Polymerization Rate on the Concentration of the Monomer in Benzene Solution

Concentration of sodium tert-butoxide 0.0047 mol/l; Polymerization 1 with quinone 0.0023 mol/l, 2 without quinone.

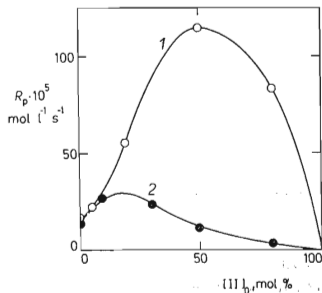


FIG. 2

Effect of Concentration of p -Benzoquinone (II) on the Polymerization Rate of Methyl Methacrylate in Benzene

Monomer concentration 2.808 mol/l; II_0 related to the concentration of sodium tert-butoxide: 1 0.0141 mol/l, 2 0.0042 mol/l.

At a concentration of *II* higher than half its value and smaller than the total concentration the polymerization occurs at a lower rate, since the content of the initiator which did not react with quinone and is able to initiate polymerization is smaller. At a lower concentration of *I* (0.1–0.2 mol.% per monomer) the polymerization rate attains the maximum value if *II* is used in a concentration of about 20 mol. % per *I*. A cause of this change in the position of the maximum can be seen in the fact that a part of butoxide which is consumed by the possible trace impurities and side reactions is in this case relatively larger with respect to its total content (but absolutely the same as at higher concentrations of *I*); consequently, the remaining amount of tert-butoxide, free to be used by the initiation of polymerization, is smaller.

For all preceding polymerizations, the following dosing order of the components was preserved: benzene, initiator, monomer with the corresponding amount of *p*-benzoquinone. Consequently, the reaction between the initiator *I* and the monomer occurred at the same time as the reaction of *I* with quinone *II*. The character of the

TABLE II
Catalytic Activity of the Reaction Product between Sodium Tert-butoxide (*I*) and Quinone (*II*)

I_0	II_0	I_0/II_0	Monomer mol/l	Time min	Conversion %
0.0936	0.0470	2	9.36	20	66
0.0468	0.0235	2	9.36	20	84
0.0094	0.0047	2	9.36	20	59
0.0468	0.0470	1	9.36	2 400	0 ^a
0.0093	0.0046	2	4.68	2	70
0.040	0.043	0.9	7.95	2 400	0
0.040	0.034	1.2	7.95	6	70

^a After an increase in I_0 to 0.056 mol/l the polymerization occurred to 84% conversion.

TABLE III
Effect of Order and Time of Dosing of Components on Polymerization Rate (R_p)
Concentration of compounds (mol/l); monomer 2.81; initiator (*I*) 0.00475; *p*-benzoquinone (*II*) 0.00237; τ dosing time of monomer.

Dosing order	Benzene, <i>I</i> , Monomer <i>II</i>			Benzene + <i>II</i> , <i>I</i> , Monomer
	60	30	8	8
τ_s, s				
$R_p \cdot 10^5, \text{mol l}^{-1} \text{s}^{-1}$	2.1	8.1	20.7	6.0

conversion curves was in these cases similar to the polymerization with alkoxide alone, showing an induction period and a sharp break of the rate according to the concentration conditions. If the components of the polymerization mixture were dosed as follows, that is, benzene with a corresponding amount of *p*-benzoquinone, initiator, monomer, with an interval of 5 min at most between the individual components, the monomer being thus added to the already formed reaction product between *I* and *II*, the conversion curves would have a somewhat different shape than in the preceding case (Table III, Fig. 3). The induction period practically disappears, and the polymerization rate is lower on the whole. A similar change in the shape of the conversion curves takes place also in the case when the original dosing order of the components is preserved, but the solution of *II* in the monomer is dosed for a longer time, *i.e.* approx. 30–60 s compared with the original 5–10 s (Fig. 4): the polymerization rate decreases with the increasing dosing time of the solutions similarly to what happens if the dosing order of the components is altered. These changes in the course of polymerization could be explained in the following way. If the monomer is added only to the reaction product of quinone and the initiator prepared in advance, the unreacted alkoxide is activated by this reaction product, and on adding the monomer the polymerization can proceed immediately without any induction period. However, a large part of the activated initiator situated inside the precipitate of the reaction

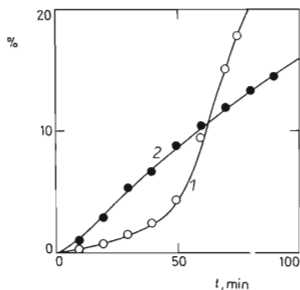


FIG. 3

Dependence of the Course of Polymerization on the Dosing Order of the Components

Concentration of components (mol/l): monomer sodium tert-butoxide (*I*) 0.00475, *p*-benzoquinone (*II*) 0.00237; dosing order: 1 benzene, *I*, monomer + *II*, 2 benzene + *II*, *I*, monomer.

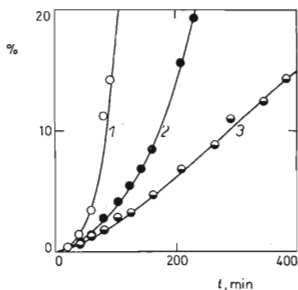


FIG. 4

Effect of the Dosing Time of Methyl Methacrylate with *p*-Benzoquinone on the Course of Polymerization

Concentration of components (mol/l): monomer 2.81; sodium tert-butoxide 0.00475; *p*-Benzoquinone 0.00237; dosing time of monomer and quinone: 1 8 s, 2 30 s, 3 60 s.

product remains inactive for polymerization (the particles of the precipitate are wrapped up in the polymer which grows on their surface), which is reflected in a considerable decrease in the polymerization rate. If the solution of *II* in the monomer is being dosed for quite a long time, the concentration of the reaction product in the reaction mixture of *II* and *I* is much lower during the dosing than half the concentration of alkoxide, so that the activation of the initiator with the monomer prevails, ensuing in a lower polymerization rate.

Microstructure of Polymers

The representation of the isotactic structure in the polymer is the higher, the higher the content of the reaction product between the initiator *I* and *p*-benzoquinone in the polymerization mixture; a change in the dosing order of the components does not affect the microstructure (Table IV). It follows from the above data that it is possible, by using quinone *II*, to influence the microstructure of the polymers obtained within quite a wide range, starting from values attained by the polymers prepared only in the presence of *I* (30–35% is-triads) to a composition which is approximately the same as that of polymers obtained when initiated with lithium catalysts (approx. 70% triads). The content of the isotactic structure in the polymer increases already after a very small addition of *II* and rises up to the abovementioned 70% of triads,

TABLE IV

Effect of Concentration of Reaction Product of Tert-butoxide (*I*) and *p*-Benzoquinone (*II*), Order and Time of Dosing of Components on Polymer Microstructure

Order of dosing: benzene, *I*, monomer + *II* (time of dosing of the last component 5–10 s, total concentration 2.81 mol/l).

<i>I</i> ₀ mol/l	<i>II</i> ₀ mol/l	Conversion %	it	Tacticity st % triads	ht
0.00237	—	31.5	37	19	44
0.00248	0.0001	24.7	40	18	42
0.00475	0.00175	18.9	47	17	36
0.00475	0.00237	19.6	51	15	34
0.0164	0.0140	80	60	14	26
0.0220	0.0196	75	70	10	20
0.0305	0.0281	78	67	10	23
0.00475	0.00237 ^a	20.0	52	16	32
0.00475	0.00237 ^a	14.8	60	13	27
0.00475	0.00237 ^b	9.6	41	19	40
0.00475	0.00237 ^c	4.0	51	15	34

^a Quinone dosed together with benzene; ^{b,c} dosing time: ^b30 s, ^c60 s.

which is attained at a quinone concentration of $2 \cdot 10^{-2}$ mol/l. It seems that a further addition of *II* above this concentration would not lead to any change in the microstructure of the polymers. It is probable that the complex of the reaction product between the initiator and *p*-benzoquinone is capable of affecting the entrance of the monomer unit into the growing chain, thus controlling propagation into higher contents of the isotactic structure.

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