Quinones as co-initiators and regulators of the polymerisation of acrylic monomers

Dmitry F. Grishin* and Aleksey A. Moykin

Research Institute for Chemistry, Nizhnii Novgorod State University, 603600 Nizhnii Novgorod, Russian Federation.
Fax: +7 8312 356 480, e-mail: chrom@nnucnit.unn.ac.ru

Systems based on quinones and trialkylboranes are efficient initiators of the polymerisation of vinylic monomers according to the 'living chain' mechanism.

Quinones are known[1] to be efficient inhibitors of the radical polymerisation of vinylic monomers. In a series of studies dealing with the polymerisation of acrylic monomers in the presence of Lewis acids,[2] including coordinatively-unsaturated organoelement compounds,[3] it has been shown that quinones and hydroquinones do not inhibit the chain growth.

In the present study we consider the radical polymerisation of methyl methacrylate (MMA) and butyl acrylate in the presence of triisobutylboron (TBB) and quinones and propose new effective coordination-radical initiators based on them.

The monomers were purified by standard procedures.[4] Triisobutylboron was synthesized by a known procedure.[5] The physicochemical parameters of all the compounds used in this study corresponded to the published data. Polymers were prepared and analysed by similar procedures.[6]

It was found that in the presence of triisobutylboron, quinones are able to initiate efficiently the polymerisation of MMA in energetically favourable regimes (Table 1). The rate of polymerisation of MMA is comparable to the rate of polymerisation of acrylic monomers in the presence of traditional radical initiators — azobisisobutyronitrile (AIBN) and acyl peroxides — and in some cases, it is even higher.

The dependence of the rate of polymerisation on the concentration of quinone is complex and passes through a maximum. For example, in the case of 3,5-di-*tert*-butyl-1,2-benzoquinone (DTBQ), the highest rate and the highest degree of conversion are observed at a [DTBQ]/[TBB] molar ratio of 0.25. In the case of benzoquinone, this occurs at a ratio of 0.5. As the concentration of the quinone is further increased, the rate of polymerisation sharply decreases. The molecular weight of the resulting polymers also decreases following an increase in the concentration of the quinone.

The overall activation energy for the polymerisation found from the Arrhenius equation (for the [DTBQ]/[TBB] ratio equal to 0.25) is 36.3 kJ mol^{-1}. This value is 2.5 times lower than the activation energy for the polymerisation of MMA in the presence of azo derivatives and peroxides (*ca.* 86 kJ mol^{-1}) and is commensurable with the corresponding parameters for the polymerisation of acrylic monomers in the presence of redox systems.[7]

Table 1 The influence of added quinones on the rate of polymerisation, molecular weight and the maximum degree of conversion of methyl methacrylate in the presence of triisobutylboron [TBB] = 0.4 mol%, T = 313 K.

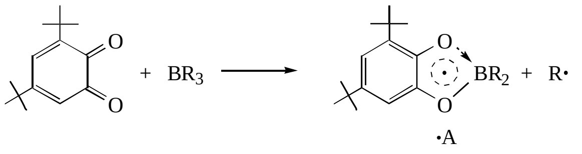
Additive	mol%	Polymerisation rate/ 10^{-4} mol dm^{-3} s^{-1}	Molecular weight	Degree of conversion after 6 h (%)
AIBN	0.1	2.2	660000	gel effect
DTBQ	0.05	2.52	348000[a]	36
	0.1	3.40	190000	32
	0.15	1.14	133000	27
	0.2	1.02	—	23
	0.3	0.51	45800	17
	0.4	0.24	24100	—
Benzoquinone	0.1	1.30	32000	18
	0.2	1.70	19500	19
	0.3	2.10	17300	28
	0.4	1.10	12500	18
	0.6	1.05	—	6
None	—	—	1700000	3

[a] The molecular weight for a degree of conversion of 16%.

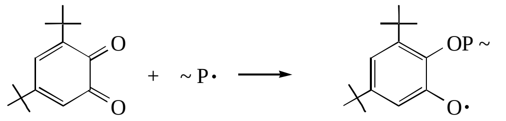
It should be noted that in the case of benzoquinone, the rate of polymerisation decreases with time, which can be due to exhaustion of one of the components of the initiating system (most likely, the quinone). This is also indicated by the fact that the colour of the polymerisation system gradually changes (when the quinone is exhausted and the solution becomes colourless, polymerisation stops).

Unlike polymerisation of MMA initiated by the systems under consideration, which occurs without gelation, polymerisation of butyl acrylate initiated by these systems proceeds to a degree of conversion of 6%, which is attained over a period of 90 s, and then the gel effect is observed. This can be attributed to the fact that the reactivities of butyl acrylate and of the corresponding chain-growth radicals are higher than those in the case of MMA and also to the fact that TBB accelerates polymerisation of acrylates, because it directly participates in chain growth.[6]

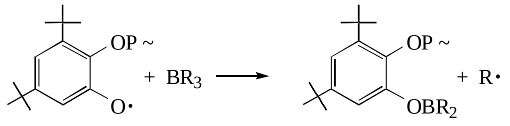
The above results indicate that several processes occur in the system. On the one hand, quinone reacts with triisobutylboron, which results in the generation of chain-propagating radicals [equation (1)]. The occurrence of reactions of this type has been assumed previously[8] based on the results of an EPR study on the interaction of trialkylboron with quinones. On the other hand, the chain-growth radicals can react with quinones to give oxygen-centred radicals of the phenoxyl type; the latter react with TBB generating new alkyl radicals,[9] which initiate polymerisation, where P is the chain-growth (polymeric) radical.



(1)



(2)

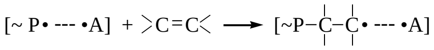


(3)

The molecular weight of poly(methyl methacrylate) synthesized in the presence of the DTBQ–TBB system depends linearly on the degree of conversion and varies over a wide range, from 17 000–200 000 (Figure 1). In the case of benzoquinone this dependence is much less pronounced. Variation of the molecular weight of a polymer as a function of the degree of conversion is usually observed for processes occurring by the mechanism of quasi-living chains,[10,11] including those carried out in the presence of iniferters. Iniferters[10] are initiators of a new type, which decompose to give an active radical capable of initiating the process and a stable radical, which can be involved only in chain termination. It can be seen from equation (1) that interaction of the components of the binary initiator, DTBQ–TBB, gives an active alkyl radical (R) able to initiate polymerisation and a stable radical (A), which can be coordinated to the chain-growth radical:

$$\sim \mathrm{P}\bullet + \bullet\mathrm{A} \longleftrightarrow [\sim \mathrm{P}\bullet \text{---} \bullet\mathrm{A}] \qquad (4)$$

The polymeric chain grows by a stepwise mechanism including consecutive acts of cleavage of the terminal labile bond (~ P• --- •A) and addition of several monomeric units to give a new labile bond, according to equation (5).


$$[\sim \mathrm{P}\bullet \text{---} \bullet\mathrm{A}] + {>}\mathrm{C{=}C}{<} \longrightarrow [\sim \mathrm{P{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}}\bullet \text{---} \bullet\mathrm{A}] \qquad (5)$$

Thus, binary compositions based on quinones and triisobutylboron are original initiating systems for the polymerisation of acrylic monomers, the chain growth during this process occurring by the mechanism of ‘quasi-living chains’.

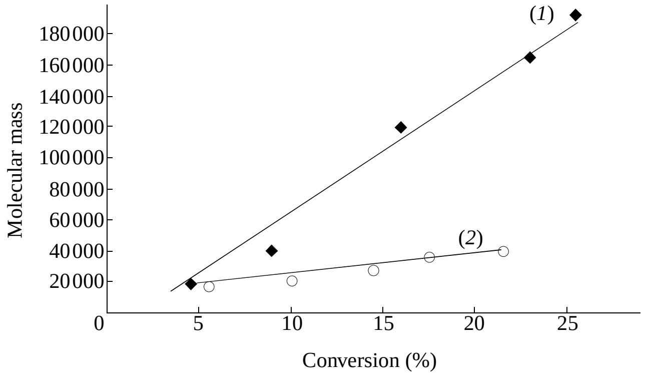


Figure 1 Dependence of the molecular weight of poly(methyl methacrylate) on the degree of conversion; $T = 313$ K, initiator: *1*, TBB + DTBQ; *2*, TBB + benzoquinone. The concentration of TBB is 0.4 mol%, that of DTBQ and benzoquinone is 0.1 mol%.

This work was supported by the Russian Foundation for Basic Research (grant no. 97-03-32823a).

The authors wish to thank Professor V. K. Cherkasov, who kindly provided DTBQ for this study.

References

1 G. Moad and D. H. Solomon, *The Chemistry of Free Radical Polymerization*, Pergamon, Oxford, 1995.

2 V. A. Kabanov, V. P. Zubov and Yu. D. Semchikov, *Kompleksno-radikal’naya polimerizatsiya* (*Complex-Radical Polymerisation*), Khimiya, Moscow, 1987, p. 256 (in Russian).

3 D. F. Grishin, *Usp. Khim.*, 1993, **62**, 1007 (*Russ. Chem. Rev.*, 1993, **62**, 951).

4 *Analytical Chemistry of Polymers*, ed. G. M. Kline, J. Wiley, New York, 1961.

5 M. F. Lappert, *The Chemistry of Boron and its Compounds*, ed. E. L. Muefferties, J. Wiley, New York, 1967, p. 433.

6 D. F. Grishin and A. A. Moikin, *Vysokomol. Soedin., Ser. B*, 1996, **38**, 1909 (in Russian).

7 J. Odian, *Principles of Polymerisation*, McGraw-Hill, New York, 1970.

8 V. A. Kondin, V. N. Alyasov, V. K. Cherkasov, V. P. Maslennikov and G. A. Abakumov, *Zh. Obshch. Khim.*, 1988, **58**, 583 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1988, **58**, 513].

9 D. F. Grishin and S. A. Vashurina, *Vysokomol. Soedin., Ser. B*, 1993, **35**, 1238 (in Russian).

10 S. S. Kuchanov, M. Yu. Zaremskii, A. V. Olenin, E. S. Garina and V. B. Golubev, *Dokl. Akad. Nauk SSSR*, 1989, **309**, 371 [*Dokl. Chem.* (*Engl. Transl.*), 1989, 335].

11 D. Braun, *Angew. Makromol. Chem*., 1994, **223**, 69.

Received: Moscow, 16th June 1997
Cambridge, 28th August 1997; Com. 7/04825D