Russian Journal of Applied Chemistry, Vol. 76, No. 3, 2003, pp. 460–463. Translated from Zhurnal Prikladnoi Khimii, Vol. 76, No. 3, 2003, pp. 475–478.
Original Russian Text Copyright © 2003 by Ergozhin, Mukhitdinova, Shoinbekova, Nikitina, Nuranbaeva.

Kinetics of Radical Polymerization of a Monomer Derived from Monoethanolamine Vinyl Ether and 1,4-Benzoquinone: A Polarographic Study

E. E. Ergozhin, B. A. Mukhitdinova, S. A. Shoinbekova, A. I. Nikitina, and B. M. Nuranbaeva

Bekturov Institute of Chemical Sciences, Ministry of Education and Science of the Kazakhstan Republic, Almaty, Kazakhstan

Received February 27, 2002

Abstract—Radical polymerization of a disubstituted monomer derived from monoethanolamine vinyl ether and 1,4-benzoquinone was studied by classical polarography. The optimal conditions for the synthesis of the redox polymer were found. The polymerization rate constants, preexponential term in the Arrhenius equation, and activation energy were calculated.

The versatility of redox and ion-exchange polymers, on the one hand, and the limited range of monomers suitable for their synthesis, on the other hand, require more intense studies in this field, with the aim to develop novel sorption processes [1, 2]. The problem of preparing new redox monomers from cheap and readily available precursors remains very urgent, since the available redox resins do not always meet the existing requirements. Among promising precursors are quinones, which widely occur in the nature and are fairly comprehensively studied. Previously [1–5] we described redox polymers based on various quinones and prepared by chemical modification of polystyrene and styrene–diene copolymers with quinones, di- and trihydroxybenzenes, and their halo derivatives.

With the aim to extend the assortment of redox resins and simplify their preparation, we developed a procedure for single-stage synthesis of new unsaturated monomers [6] from readily available and cheap monoethanolamine vinyl ether (MEAVE) and various quinones. This reduced the cost of redox ion exchangers and made their production profitable; the capability for reversible oxidation–reduction allows repeated use of these resins, which is important for commercial applications.

One of reliable, highly sensitive, and quick methods for analysis of macromolecular compounds is polarography. It is widely used in kinetic studies of polymerization of vinyl monomers [7–12]. It is known that the principal characteristic of the reactivity of unsaturated monomers is the polymerization rate constant. However, only in a few papers [12–14] this quantity was determined polarographically. The relationship between the rate constants of radical polymerization of monomers and the potentials of the half-waves of their reduction on a mercury dropping electrode were established in [13].

In this work we studied by classical polarography the kinetics of radical polymerization of a disubstituted monomer derived from MEAVE and 1,4-benzoquinone (MEAVE–1,4-BQ), calculated the polymerization rate constants at various temperatures, the activation energy, and the preexponential term in the Arrhenius equation.

EXPERIMENTAL

Monoethanolamine vinyl ether was dried over freshly distilled K_2CO_3 and distilled from calcium hydride; bp 114°C, n_D^{20} 1.4382.

1,4-Benzoquinone (pure grade) was recrystallized from methanol; mp 116°C after purification.

Azobis(isobutyronitrile) (AIBN) was recrystallized from absolute methanol; mp 102–103°C.

The monomer, 2,5-bis[*N*-(2-vinyloxy)ethyl]amino-1,4-benzoquinone $C_{14}H_{18}N_2O_4$, was prepared as follows. MEAVE was added in 6 : 1 ratio to a solution of 1,4-BQ in 1,4-dioxane (28.2 g l^{-1}, or 0.26 M) at 25°C with continuous stirring. After 15 min, distilled

Table 1. Elemental composition and some physicochemical properties of the monomer derived from MEAVE and 1,4-BQ and of its polymer

Compound	Calculated, %/Found, %				Yield, %	T_m, °C	[η],* dl g^{-1}	ρ,** g cm^{-3}	SEC**	ROC***
	C	H	N	O					mg-equiv g^{-1}	
Monomer	60.43/60.47	6.47/6.58	10.07/11.08	23.03/12.87	62.36	172–175	–	0.4442	–	–
Polymer	60.43/60.49	6.47/6.49	10.07/11.00	23.03/22.02	67.80	216–218	0.43	1.0714	8.7	4.2

* The intrinsic viscosity was determined at 25°C in DMF.
** The density and static exchange capacity were determined according to [15].
*** The redox capacity was determined according to [1].

water was added, the precipitate was filtered off, reprecipitated, and dried first in air and then in a vacuum oven at 40–50°C to constant weight. The chemical composition and some physicochemical properties of the MEAVE–1,4-BQ are listed in Table 1.

Polymerization of MEAVE–1,4-BQ was performed as follows. AIBN, 1–7 wt % relative to the monomer, was added into an ampule containing a solution of the monomer in dimethylformamide (DMF; 0–44 g l^{-1}). The ampule was purged with argon, sealed, thoroughly shaken, and placed in a thermostat heated to 55–75°C. After reaction completion, the ampule was quickly transferred in a beaker filled with ice, cooled, and opened. The precipitate was filtered off and dried first in air at 20–25°C and then in a vacuum oven at 40–50°C. The polymer yield was 50.0–67.8%. The optimal conditions are as follows: monomer concentration in DMF 25 g l^{-1} (0.0899 M); AIBN amount 5 wt % relative to the monomer (1.25 g l^{-1}, or 0.762×10^{-2} M); 68°C; 120 min. The main physicochemical characteristics of the polymer are given in Table 1.

The IR spectra of the new quinoid derivative of MEAVE contains the following absorption bands, cm^{-1}: NH stretching 3256; NH bending 1552; C=O stretching 1660; C=C stretching 1568, 1440; =C–N stretching 1328; and C–O–C stretching 1200. The absorption band of quinoid rings in the spectrum of the polymer becomes broader, which is typical of polymeric quinones, and these bands are shifted toward higher frequencies to 1680 cm^{-1}. The bands at about 3040 cm^{-1} characteristic of the vinyl group disappear, whereas the bands at 2936 and 1496 cm^{-1} belonging to the $-CH_2-$ groups grow in intensity.

The polarograms were taken in a temperature-controlled cell at 25±0.5°C with a PU-1 polarograph equipped with a mercury dropping electrode having the open-curcuit capillary characteristic $m^{2/3}t^{1/6}$ = 4.38 mg$^{2/3}$ s$^{1/2}$. As reference electrode was used saturated calomel electrode. Prior to polarographic measurements, the solutions were purged with argon to remove oxygen. The half-wave potentials were determined by graphic solution of the wave equation in the coordinates $\log i/(I - i)$ vs. E, where i is the current at voltage E and I is the diffusion current [16, 17].

Experiments on studying the kinetics of radical polymerization of the new disubstituted redox monomer based on MEAVE and 1,4-BQ, 2,5-bis[*N*-(2-vinyloxy)ethyl]amino-1,4-benzoquinone (MEAVE–1,4-BQ), were performed as described above; after a certain time, the ampules were successively opened, and samples were taken for polarographic analysis. The samples were diluted with DMF to stop the reaction. Polarographic measurements were performed in 25% DMF, with phosphate buffer solution (pH 7.4) as supporting electrolyte. The conversion was judged from the amount of the unchanged monomer. Experiments revealed a linear relationship between the heights of the polarographic waves and the monomer concentration in the solution. The monomer content was determined from the calibration plot.

Analysis of the reaction mixture furnished information on the degree of conversion and allowed construction of the polymerization curves (Fig. 1).

To calculate the overall polymerization rate constants, we determined the reaction order. The logarithmic dependence of the polymerization rate on the initiator concentration (Fig. 2) and the linear depen-

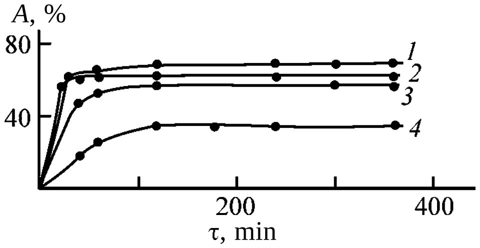

Fig. 1. Kinetic curves of MEAVE–1,4-BQ polymerization: (*A*) polymer yield and (τ) time. Temperature, °C: (*1*) 68, (*2*) 75, (*3*) 62, and (*4*) 55.

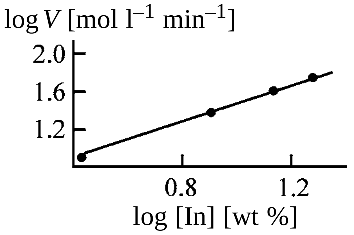

Fig. 2. Logarithmic plot of the polymerization rate, log *V*, vs. initiator concentration log [In].

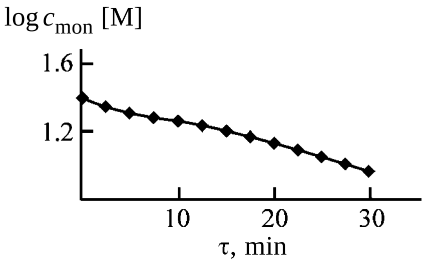

Fig. 3. Plot of log c_{mon} vs. time τ of MEAVE–1,4-BQ polymerization.

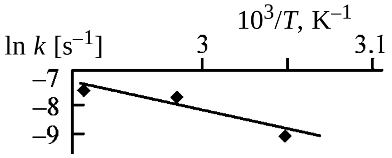

Fig. 4. Logarithm of the rate constant ln *k* of MEAVE–1,4-BQ polymerization as a function of temperature *T*.

dence of log *c* of the monomer on the reaction time (Fig. 3) show that the reaction is first-order with respect to the initiator (n = 0.80) and monomer (m = 0.86) and is described by relationships characteristic of first-order reactions.

The rate constants of MEAVE–1,4-BQ polymerization calculated by the first-order kinetic equation [18, 19] and the preexponential terms k_0 in the Arrhenius equation $k = k_0e^{-E/RT}$ are listed in Table 2.

The plot of ln *k* vs. 1/*T* is a straight line; from its slope, we determined the activation energy of the process, $E = 4.57|\tan\alpha|\xi$, where α is the slope of the straight line and ξ is the scale ratio of the abscissa and ordinate (Fig. 4).

Table 2. Kinetic characteristics of polymerization of the monomer based on MEAVE–1,4-BQ

T, K	$10^3/T$, K^{-1}	$k \times 10^4$, s^{-1}	$\ln k$	$k_0 \times 10^{15}$, s^{-1}
328	3.05	1.22	–9.015	1.379
335	2.99	3.72	–7.898	1.681
341	2.93	5.38	–7.530	1.141
348	2.87	5.48	–7.508	0.498

In the chosen scale, tan α = tan 32° = 0.6249, ξ = 10^3, and activation energy $E = 4.571 \times 0.6249$ = 2.86 kcal mol^{-1} (11.95 kJ mol^{-1}).

The synthesized disubstituted monomer derived from MEAVE and 1,4-BQ readily polymerizes, in contrast to the starting MEAVE, which, as reported in [20, 21], does not form homopolymers in the presence of radical initiators. Apparently, this is due to the reactivity of the radical, which is the decisive factor in homopolymerization. The higher the electron density localized on the double bond, the more reactive is the monomer [7, 10]. The polarographic parameters are also determined by the electron density localized on the double bond: the higher the electron density, the more negative is the half-wave potential of the reduction of the double bond, i.e., the more negative the potential, the readier is the polymerization, which is indeed the case with MEAVE–1,4-BQ.

CONCLUSIONS

(1) Radical polymerization of the new disubstituted derivative based on monoethanolamine vinyl ether and 1,4-benzoquinone was studied, and optimal conditions were found for formation of the polymeric redox resin.

(2) The kinetics of radical homopolymerization was studied, and the rate constants, activation energy, and preexponential term in the Arrhenius equation were calculated.

REFERENCES

1. Ergozhin, E.E. and Mukhitdinova, B.A., *Redoksionity* (Redox Ion Exchangers), Alma-Ata: Nauka, 1983.
2. Ergozhin, E.E. and Mukhitdinova, B.A., *Okislitel'no-vosstanovitel'nye ionoobmenniki* (Redox Ion Exchangers), Almaty: Redaktsionno-Izd. Otd., Vyssh. Attest. Komissiya Resp. Kazakhstan, 2000.
3. Ergozhin, E.E., Mukhitdinova, B.A., Bakirova, R.Kh., *et al.*, *React. Polym.*, 1991/1992, vol. 16, pp. 321–334.
4. Ergozhin, E.E., Mukhitdinova, B.A., and Dusenbenova, Z.K., *React. Polym.*, 1992, vol. 18, pp. 15–23.
5. Ergozhin, E.E., Mukhitdinova, B.A., Dusenbenova, Z.K., *et al.*, *Polymer*, 1993, vol. 34, no. 14, pp. 3096–3106.
6. Shoinbekova, S.A., New Nitrogen-Containing Redox Monomers and Polymers Based on Them, *Cand. Sci. Dissertation*, Almaty, 1999.
7. Bezuglyi, V.D., *Polyarografiya v khimii i tekhnologii polimerov* (Polarography in the Polymer Chemistry and Technology), Moscow: Khimiya, 1968.

8. Shur, A.M., Filimonov, B.F., and Filimonova, M.M., *Vysokomol. Soedin.*, 1961, vol. 3, no. 11, pp. 1661–1663.
9. Bobrova, M.N. and Matveeva, A.N., *Zh. Obshch. Khim.*, 1956, vol. 26, no. 7, pp. 1857–1860.
10. Bezuglyi, V.D. and Dmitrieva, V.N., *Zh. Prikl. Khim.*, 1957, vol. 30, no. 5, pp. 744–750.
11. Bezuglyi, V.D., Alekseeva, T.A., and Dmitrievskaya, L.I., *Vysokomol. Soedin., Ser. A*, 1967, vol. 7, no. 5, pp. 1185–1189.
12. Ergozhin, E.E., Mukhitdinova, B.A., Shoinbekova, S.A., *et al.*, *Zh. Prikl. Khim.*, 2001, vol. 74, no. 11, pp. 1847–1849.
13. Alekseeva, T.A., Bezuglyi, V.D., Dmitrieva, V.N., *et al.*, *Vysokomol. Soedin.*, 1963, vol. 5, no. 9, pp. 1382–1387.
14. Bezuglyi, V.D., Alekseeva, T.A., Dmitrievskaya, L.I., *et al.*, *Vysokomol. Soedin.*, 1964, vol. 6, no. 1, pp. 125–129.
15. Toroptseva, A.M., Belogorodskaya, K.V., and Bondarenko, V.M., *Praktikum po khimii i tekhnologii vysokomolekulyarnykh soedinenii* (Practical Course of Chemistry and Technology of Macromolecular Compounds), Leningrad: Khimiya, 1972.
16. Mairanovskii, S.G., Stradyn', Ya.P., and Bezuglyi, V.D., *Polyarografiya v organicheskoi khimii* (Polarography in Organic Chemistry), Leningrad: Khimiya, 1975.
17. Heyrovsky, J. and Kuta, J., *Zaklady polarografie*, Prague: Ceskoslov. Acad. Ved, 1962.
18. Panchenkov, G.M. and Lebedev, V.P., *Khimicheskaya kinetika i kataliz* (Chemical Kinetics and Catalysis), Moscow: Mosk. Gos. Univ., 1961.
19. Emanuel', N.M. and Knorre, D.G., *Kurs khimicheskoi kinetiki* (Course of Chemical Kinetics), Moscow: Vysshaya Shkola, 1974.
20. Shostakovskii, M.F. and Chekulaeva, I.A., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1953, no. 2, pp. 368–373.
21. Nurkeeva, Z.S. and Seitov, A.Z., in *Radiatsionnye effekty v geterogennykh sistemakh* (Radiation Effects in Heterogeneous Systems), Alma-Ata: Gylym, 1983, pp. 63–68.