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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Kinetics of Polycondensation of Allyl Bromide and Monoethanolamine Vinyl Ether with Resorcinol Diglycidyl Ether

K. Kh. Khakimbolatova, E. E. Ergozhin, T. K. Chalov, T. V. Kovrigina, and A. I. Nikitina

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

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Abstract—Polycondensation of resorcinol diglycidyl ether, monoethanolamine vinyl ether, and allyl bromide in dimethylformamide solution was studied. The kinetic parameters of the process were determined.

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The use of epoxy and allyl compounds allows production of polymers with longer service life, due to improved physicomechanical properties and enhanced resistance to heat and chemicals. This particularly concerns ion-exchange materials which in the course of operation are in contact with oxidants, acids, or alkalis. Therefore, search for new synthetic routes to ion exchangers based on allyl and epoxy monomers is a topical problem.

Previously we prepared various polyfunctional anion exchangers derived from allyl halides, diglycidyl ethers of benzenediols, and di- and polyamines [1–3], and also from allyl bromide (AB), epichlorohydrin oligomer, and polyethylenimine [4]. The structure of reactants significantly affects the cell size in three-dimensional ion exchanger networks, which, in turn, affects the degree of recovery of various metal ions. In particular, network anion exchangers prepared from allyl bromide, resorcinol diglycidyl ether (RDGE), and polyethylenepolyamine efficiently sorb transition metal ions [3]. The use of monoethanolamine vinyl ether (MEAVE) for their synthesis is due to the fact that this is a proton-donor compound, and such compounds are known [5] to activate the epoxy ring. Furthermore, incorporation of MEAVE, which contains nitrogen and oxygen atoms bearing lone electron pairs, into anion exchangers should enhance their complexing ability. We have developed a procedure for preparing new polyelectrolytes by condensation of RDGE, MEAVE, and AB, followed by their thermal curing with hexamethylenediamine (HMDA).

This study concerns kinetic features of polycondensation of resorcinol diglycidyl ether, monoethanolamine vinyl ether, and allyl bromide.

EXPERIMENTAL

Allyl bromide was of chemically pure grade, n_D^{20} 1.4690, bp 71.3°C. Resorcinol diglycidyl ether was distilled at 80°C/20 mm Hg. Monoethanolamine vinyl ether was treated with sodium metal and distilled with collection of the fraction boiling at 114°C, n_D^{20} 1.4382 [6].

Pure grade dimethylformamide (DMF) was dried over calcium hydride and distilled at 44–45°C/15 mm Hg; n_D^{20} 1.4300 (bp 153°C, n_D^{20} 1.4300 [7]).

Polycondensation of RDGE, MEAVE, and AB was performed at their weight ratio of 1 : 1 : 1, allowing preparation of the ion exchangers in the highest yield, in DMF at 70–80°C. The reaction time was varied from 15 min to 5 h. At definite intervals, samples of the reaction mixture were withdrawn and multiply diluted DMF to fully stop the reaction. Then the content of AB ($E_{1/2}$ –1.41 V) and MEAVE ($E_{1/2}$ –1.97 V) was determined by classical polarography using as supporting electrolyte 0.2 M LiCl in 50% DMF. Under these conditions, RDGE is polarographically inactive. Therefore, the reaction order was determined only with respect to AB and MEAVE concentrations.

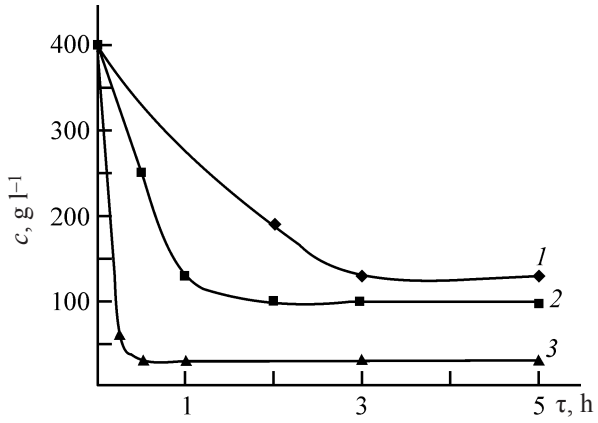


Fig. 1. Kinetic curves of the reaction of AB with RDGE and MEAVE. (*c*) Concentration and (τ) time; the same for Fig. 2. *T*, °C: (*1*) 70, (*2*) 75, and (*3*) 80; the same for Fig. 2.

The polarograms were taken with a PU-1 polarograph in a temperature-controlled cell at 25 ± 0.2°C, with saturated calomel reference electrode. The solutions prior to polarographic measurements were deoxygenated by passing argon for 5 min.

Despite wide use of allyl and especially epoxy compounds, only a few papers deal with kinetic features of reactions involving them [5, 8, 9]. The mechanism of polycondensation of epoxy monomers and amines is fairly complex and becomes even more complex on introducing a third reactant into the reaction system. At the same time, detailed study of the kinetics of the reactions involving RDGE, MEAVE, and AB present in the ternary system would be useful not only for quantitatively describing the process, but also for controlling it using the kinetic data obtained.

In studying kinetic characteristics of virtually all chemical reactions, one of important experimental problems is to determine how the concentrations of separate components of the reaction mixture vary with time. Both chemical and physical methods of analysis are used for this purpose. The most convenient of them is classical polarography [10, 11] whose advantages are versatility, experimental simplicity, ease of interpretation of experimental data, and relatively high accuracy. Therefore, when studying the kinetics of the reaction of RDGE, MEAVE, and AB, we used the polarographic method allowing simultaneous determination of the concentrations of two components, AB and MEAVE, from one sample of small volume.

Figures 1 and 2 show the kinetic curves of AB and MEAVE consumption in their reaction with RDGE. As can be seen, with an increase in the time and temperature of polycondensation of RDGE, MEAVE, and AB, the concentrations of AB and MEAVE in the reaction mixture decrease. In the reaction of RDGE, the MEAVE conversion is 75%, and the AB conversion, 92%, whereas it was found [4] that the conversion of AB in the reaction with epichlorohydrin oligomer did not exceed 40%. As we suggested, the epoxy ring of RDGE is apparently activated by monoethanolamine vinyl ether, which is a proton-donor compound [5].

As follows from [12], the reaction order with respect to particular reactant is more interesting and more important than the overall reaction order. The reaction order with respect to AB and MEAVE concentrations was found by the integral method [13], by plotting $\ln(c/c_0)$ vs. time, where c_0 is the initial, and c, the running concentration of AB or MEAVE. It follows from the linear dependences obtained, which pass through the origin (Fig. 3), that the reaction of both AB and MEAVE with RDGE in the initial period is first-order with respect to the AB and MEAVE concentrations. Therefore, the rate constants *k* were calculated by the first-order rate equation [14]. The apparent activation energies (see table) were determined from the Arrhenius dependences (Fig. 4).

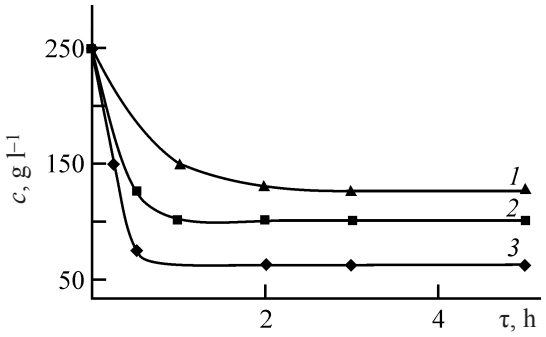


Fig. 2. Kinetic curves of the reaction of MEAVE with AB and RDGE.

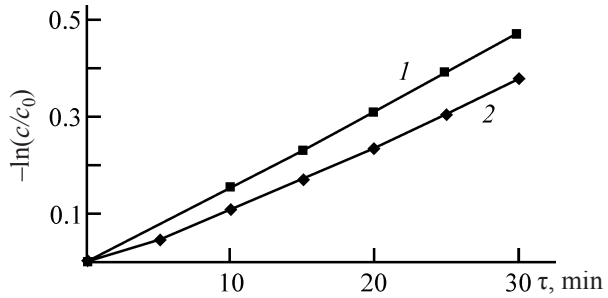
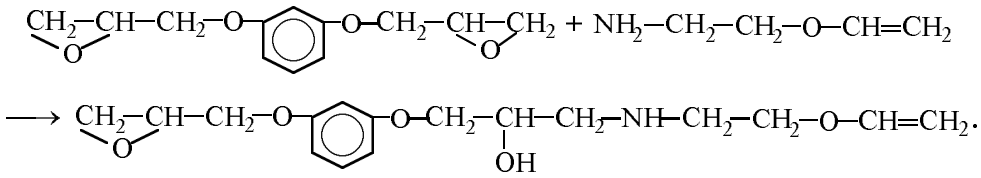
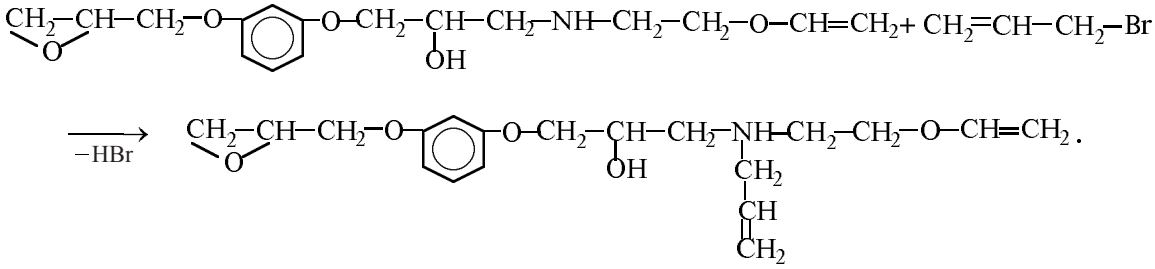


Fig. 3. Plots of $\ln(c/c_0)$ vs. time τ of the reactions of (*1*) MEAVE and (*2*) AB with resorcinol diglycidyl ether.

As seen from the table, the activation energy of the reaction of AB with RDGE is approximately 2.5 times higher than that of the reaction of MEAVE with RDGE. Therefore, first RDGE reacts with MEAVE:

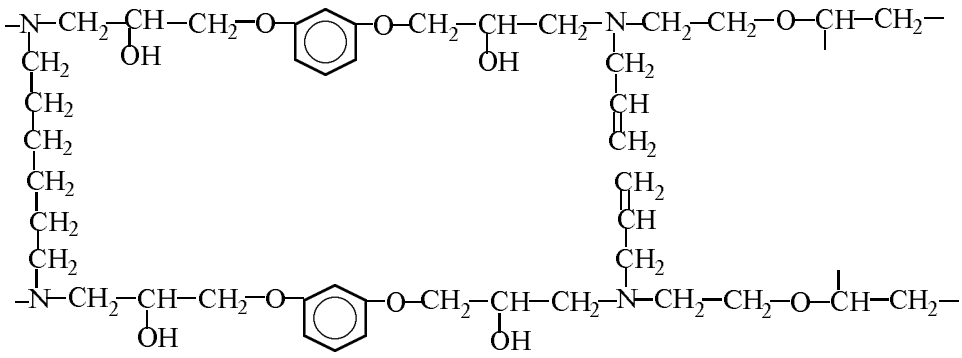


The resulting product then reacts with allyl bromide with the release of HBr:



Addition of HMDA in the second step leads to complete curing due to the reaction of HMDA with the remaining epoxy groups, with the formation of a net-work anion exchanger, presumably of the following structure:

Our results indicate that, under the optimal conditions (80°C, 30 min), the major fraction of MEAVE and allyl bromide reacts with RDGE.



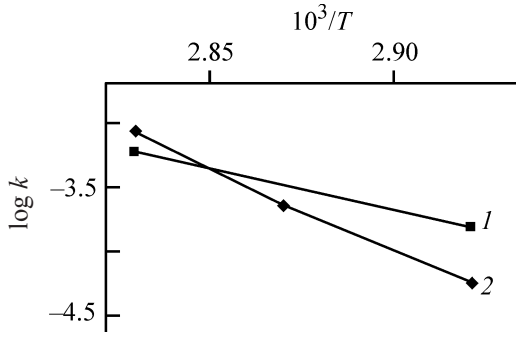


Fig. 4. Arrhenius plots for the reactions of (*1*) MEAVE and (*2*) AB with resorcinol diglycidyl ether. (*T*) Temperature.

CONCLUSIONS

(1) The polycondensation of resorcinol diglycidyl ether, monoethanolamine vinyl ether, and allyl bromide

Kinetic characteristics of the reaction of AB and MEAVE with RDGE

Monomer	T, K	$k \times 10^4$, s^{-1}	E_{act}, kJ mol^{-1}
AB	343	0.53	
	348	2.23	253.48
	353	8.12	
MEAVE	343	1.42	
	348	3.19	96.42
	353	5.75	

in the initial period is a first-order reaction with respect to the concentrations of AB and MEAVE.

(2) The rate constants and activation energies of the reactions of monoethanolamine vinyl ether and allyl bromide were calculated.

REFERENCES

1. Ergozhin, E.E., Chalov, T.K., Iskakova, R.A., et al., *Zh. Prikl. Khim*., 2002, vol. 75, no. 1, pp. 103–106.
2. Ergozhin, E.E., Chalov, T.K., Iskakova, R.A., and Sarsenov, S.K., *Zh. Prikl. Khim.,* 2002, vol. 75, no. 11, pp. 1826–1829.
3. Ergozhin, E.E., Chalov, T.K., Kovrigina, T.V., et al., *Zh. Prikl. Khim*., 2004, vol. 77, no. 10, pp. 1693–1698.
4. Chalov, T.K., Ergozhin, E.E., Nikitina, A.I., et al., *Zh. Prikl. Khim*., 2007, vol. 80, no. 11, pp. 1878–1881.
5. Mutin, I.I., Arutyunyan, Kh.A., Davtyan, S.P., and Rozenberg, B.A*., Kinet. Katal*., 1979, vol. 20, no. 6, pp. 1567–1570.
6. Shostakovskii, M.F., *Prostye vinilovye efiry* (Vinyl Ethers), Moscow: Akad. Nauk SSSR, 1952.
7. Weissberger, A. and Proskauer, E.S., *Organic Solvents. Physical Properties and Methods of Purification*, Riddick, J.A. and Toops, E.E., Eds., New York: Interscience, 1955.
8. Blyakhman, E.M., Nikitina, A.A., Zelenina, N.L., and Shevchenko, Z.A., *Vysokomol. Soedin*., 1974, vol. 16, no. 5, pp. 1031–1036.
9. Blyakhman, E.M., Shevchenko, Z.A., and Alekseeva, E.L., *Vysokomol. Soedin*., 1976, vol. 18, no. 10, pp. 2208–2211.
10. Bezuglyi, V.D., *Polyarografiya v khimii i tekhnologii polimerov* (Polarography in Polymer Chemistry and Technology), Leningrad: Khimiya, 1968.
11. Mairanovskii, S.G., *Kataliticheskie i kineticheskie volny v polyarografii* (Catalytic and Kinetic Waves in Polarography), Moscow: Nauka, 1966.
12. Sykes, P., *A Guidebook to Mechanism in Organic Chemistry*, New York: Longman, 1986.
13. Berlin, A.A., Vol'fson, S.A., and Enikolopyan, N.S., *Kinetika polimerizatsionnykh protsessov* (Kinetics of Polymerization Processes), Moscow: Khimiya, 1978.
14. Emanuel', N.M. and Knorre, D.G., *Kurs khimicheskoi kinetiki* (Course of Chemical Kinetics), Moscow: Vysshaya Shkola, 1984.