

Alkaline Hydrolysis of Ethyl Acrylate– Acrylonitrile–Divinylbenzene Copolymer Beads

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Synopsis

This article deals with the alkaline hydrolysis of ethyl acrylate–acrylonitrile–divinylbenzene copolymer beads. Chemical changes during hydrolysis were evaluated by means of determination of total weight exchange capacity and of infrared spectroscopy. The influence of reaction temperature, concentration of the hydrolytic agent, degree of copolymers crosslinking as well as the influence of particle size upon the rate of hydrolysis were studied as a function of time. The mathematical and statistical calculations of experimental data were carried out. With respect to time dependence of hydrolysis of the copolymer functional groups, the average values of reaction rate constants as well as the values of assumed diffusion coefficients were calculated. The analysis is based on partial linearization of experimental results by means of semilogarithmic transformation. The empirical relations expressing dependences of reaction rate constants and of diffusion coefficients on conditions of hydrolysis were determined.

INTRODUCTION

The alkaline hydrolysis of esters and nitriles in organic chemistry of low-molecular compounds has been well described.¹ However, this is not the case for hydrolysis of polymers containing the mentioned groups and especially for crosslinked copolymers in bead form. Let us make reference to some preceding articles. The above problems are described for instance by Smets and his co-workers,²⁻⁴ by Štamberg and Ševčík,⁵ or by Hynková and Hrabal^{6,7} as well as in patent literature.^{8,9} From the point of view of reaction kinetics the system of solid copolymer particles suspended in the liquid reaction medium is rather complicated. The reaction systems solid–liquid, especially those concerning heterogeneous catalysis, are described, e.g., by Aris,¹⁰ who deals with these questions, however, only from the theoretical point of view. He has shown that the mathematical models of reacting solids in the liquid reaction medium can be exactly used only for isolated examples with simplified assumptions. That is why we have decided to describe the obtained results by means of empirical relations applicable especially to this investigated system in the given range.

PROBLEM ANALYSIS

Contrary to the hydrolysis of monomer esters and nitriles which is affected by the reaction temperature and by the time and concentration of the hydrolytic agent, only in case of crosslinked copolymer beads there is another important factor, namely, hydrolytic agent diffusion into the mass

of the hydrophobic skeleton, which is affected by the skeleton network density and by the copolymer particle size. It means therefore that the studied questions are determined by diffusion of reaction components into copolymer particles and by subsequent chemical reaction between the liquid reagents and reactive groups fixed to the crosslinked copolymer. The subject under discussion in our case are the ester and nitrile groups hydrolyzed by the aqueous solution of sodium hydroxide.

This article represents the continuation of results obtained in case of aminolysis of similar copolymers,¹¹ and it is also based on the analogous study of nonsteady diffusion and thermal processes mentioned, e.g., in the work of Legras¹² as well as on diffusion processes combined with the chemical reaction mentioned, e.g., by Jost¹³. The authors of other studies^{14,15} analyze the nonsteady heat conduction in solid particles. They define a so-called regular regime when the initial temperature distribution as well as the initial distribution of the concentration of diffusing components in the particle in our case are no longer important and the further course of the process is controlled only by conditions on the particle surface. This phase of the process can be approximated by a straight line with the semilogarithmic transformation of time and concentration values. The initial time segment of these relations when the concentrations of diffusing reactive liquids inside and outside the copolymer particles are getting balanced is taken as the time of diffusion of the hydroxide solution into the copolymer particles. In the further course of the process the proper chemical reaction takes place—as is evident from the conversion curves. The influence of reaction conditions upon the conversion of functional groups was studied as a function of time. Semilogarithmic data transformation was used to analyze the experimental results. This makes it possible to linearize the S-shaped conversion curves for both the first phase of hydrolysis and the other one when the proper reaction occurs. The main object of this paper is the mathematical and statistical analysis of experimental data, the calculation of the average values of rate constants, as well as of the values of assumed diffusion coefficients and activation energy and the construction of empirical relations for the description of hydrolysis.

EXPERIMENTAL

Substances Used

The copolymers were prepared by suspension copolymerisation of ethyl acrylate with acrylonitrile (10 wt %) and divinylbenzene (7.8 wt % calculated for 100% substance, if not stated otherwise) initiated by azobisisobutyronitrile (0.15 wt %) in the medium of aqueous solution of gelatine (1.5 wt %), sodium chloride (10 wt %), and hydroxyethylcellulose (0.7 wt %).¹⁶ For the alkaline hydrolysis an aqueous solution of sodium hydroxide (of analytical grade purity) was used; its concentration was 35 wt %, if not stated otherwise.

Analytical Methods

The content of carboxyl groups was studied by evaluating the total content of groups which are capable of exchange by the method described in the

literature.¹⁷ The other method used for studying of changes in the content of ester, nitrile, amide, and carboxyl groups in the samples taken during hydrolysis was infrared spectroscopy carried out with dried samples in H⁺ form by KBr technique.

Eight milligrams of the sample had been ground at the temperature of liquid nitrogen for 60 min. After homogenization with 1 g KBr the infrared spectrum of pressed pellets was taken on the spectrophotometer Perkin-Elmer 283. One third from the pellet was segregated; after homogenization with KBr, another pellet was pressed, and the infrared spectrum for lower content of substance was taken. Two takes were necessary with regard to the fact that the studied absorption bands have an essentially different intensity. The used absorption bands were 2240 cm⁻¹ for nitrile groups, 1735 cm⁻¹ or 1025 cm⁻¹ (vibration of C—H bond in ethyl groups of ethyl acrylate) for ester groups, 2600 cm⁻¹ and 1705 cm⁻¹ for carboxyl groups, 1660 cm⁻¹ and 1550 cm⁻¹ for amide groups resulting from nitrile groups. It was necessary with respect to the use of KBr techniques to correlate the absorbances of the internal standard; it means the band 710 cm⁻¹ corresponding to the out-of-plane vibration of *m*-disubstituted aromatic ring in *m*-divinylbenzene. The conversion of nitrile and ester groups is expressed by the relation

$$K = \frac{a_{\tau=0} - a_{\tau}}{a_{\tau=0}} \times 100$$

where *K* represents the conversion (%) and *a*_{τ=0}, *a*_τ the relative absorbances at time τ = 0 and at time τ.

Process of Copolymer Hydrolysis

A flask provided with a stirrer, reflux condenser, thermometer (with a 0.5°C division), and contact thermometer was charged with 40 g of the wet, centrifuge separated (*G* = 1200 m · s⁻²) copolymer with a content of 7.8 wt % of divinylbenzene (calculated for 100% substance) and bead size *d* = 0.65 mm. Besides 160 mL of aqueous solution of sodium hydroxide (concentration 35 wt %) were added. The suspension had been stirred and heated for 7 h. The samples were taken at fixed time intervals.

The following relations were studied: the influence of the hydrolytic agent concentration in 3.7, 8.5, 12.5, 20.0, 27.2, 32.5 wt % of sodium hydroxide; the influence of the reaction temperature in the interval from 86.5°C to 106°C at constant concentration and quantity of hydrolytic agent; the influence of the degree of crosslinking for copolymers containing from 3.9 to 19.3 wt % of divinylbenzene (calculated for 100% substance) and the influence of bead sizes by using copolymers with an average size *d*₁ = 0.65 mm, *d*₂ = 0.9 mm, *d*₃ = 1.1 mm, *d*₄ = 1.3 mm (the range of sizes was ±10% of the middle size).

RESULTS AND DISCUSSION

The rate of copolymer bead hydrolysis increases in accordance with rising concentration of sodium hydroxide so as it is shown in Figure 1. It is evident that both the first phase of the reaction course which is determined by the

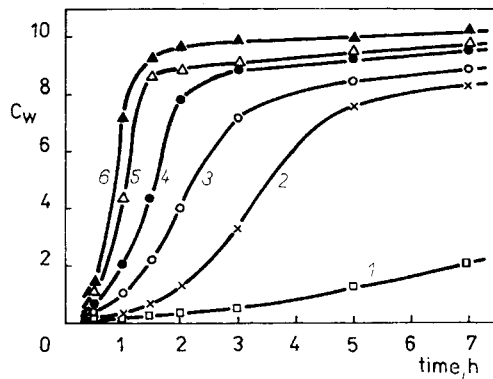


Fig. 1. Time dependence of copolymer hydrolysis on the hydrolytic agent concentration (wt % NaOH): (1) 3.7; (2) 8.5; (3) 12.5; (4) 20.0; (5) 27.2; (6) 32.5. C_w = total weight exchange capacity ($\text{mmol} \cdot \text{g}^{-1}$) of solids. Reaction temperature = 373.2 K.

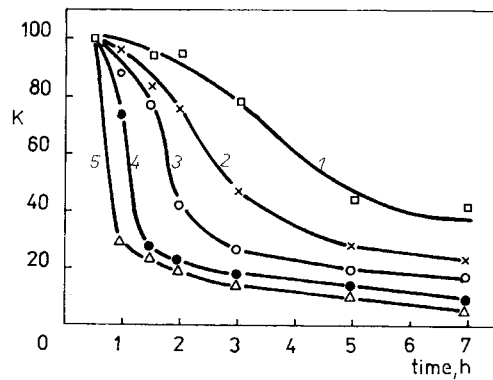


Fig. 2. Time dependence of conversion of nitrile groups on the hydrolytic agent concentration (wt % NaOH): (1) 8.5; (2) 12.5; (3) 20.0; (4) 27.2; (5) 32.5.

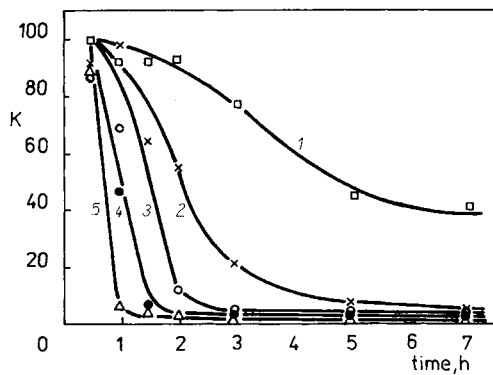


Fig. 3. Time dependence of conversion of ester groups on the hydrolytic agent concentration (wt % NaOH): (1) 8.5; (2) 12.5; (3) 20.0; (4) 27.2; (5) 32.5.

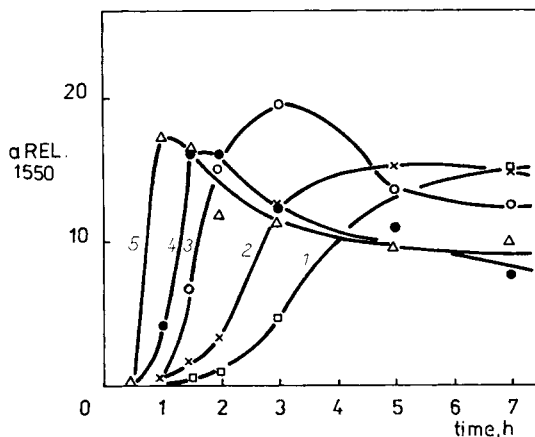
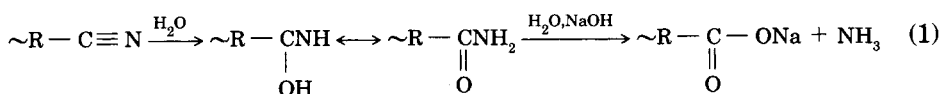


Fig. 4. Time dependence of relative absorbance at 1550 cm^{-1} (amide groups) on the hydrolytic agent concentration (wt % NaOH): (1) 8.5; (2) 12.5; (3) 20.0; (4) 27.2; (5) 32.5.

diffusion of the hydrolytic agent into the material of beads and the second one which is determined by the proper chemical conversion of the active groups of copolymer become shorter with increasing NaOH concentration. At NaOH concentrations above 20 wt % it is possible to reach in only 3 h such values of exchange capacities which come near the theoretical ones. From the graphical expression of the decrease of ester and nitrile groups (Figs. 2 and 3) it can be concluded that the ester groups decrease much faster in comparison with the nitrile ones. This demonstrates their higher reactivity which is well known from the hydrolysis of monomers. Through the course of extinction at the band 1550 cm^{-1} the formation of the amide groups was studied. It is shown in Figure 4. The curve goes through a maximum. It indicates the fact that the amide groups are intermediates in the hydrolysis of nitrile groups to carboxyl groups. It corresponds to following scheme:



Dependence of the hydrolysis course on reaction temperature (106°C , 100°C , 95°C , 90°C , 88°C , 86.5°C) has similar tendency in comparison with the previous case. The higher the temperature, the higher also are reaction rates, and the shorter are the diffusion times. From the study of conditions of the hydrolysis course for differently crosslinked copolymers, it can be concluded that in case of crosslinked copolymers with higher content of divinylbenzene the conversion decreases not only owing to increased content of divinylbenzene that has no active groups, but may be also due to the steric hindrance which makes the approach of the hydrolytic agent to active groups difficult. The bead size affects only the first phase of hydrolysis—the diffusion of the hydrolytic agent.

With regard to relative great number of data the detailed graphical evaluation was not carried out—contrary to the study of the influence of the

hydrolytic agent concentration. Mathematical and statistical evaluation was used for all the measurements and the results are presented in tables. In this connection it is necessary to point out that the evaluated system is rather complicated especially in consequence of the fact that chemical reactions on copolymers are carried out under nonsteady conditions. At the same time there occurs a change from a typical hydrophobic to a hydrophilic substance. In the following text the reaction kinetics during hydrolysis and also the diffusion of aqueous solution of sodium hydroxide into the structure of crosslinked copolymer have been described in accordance with empirical relations, which were obtained by multiple linear regression of logarithmic values of individual variables.

In the course of data processing the relations describing reactions in homogeneous systems were used.¹⁰ From this point of view the hydrolysis of ester groups must be regarded as a second-order reaction whereas the hydrolysis of nitrile and amide groups on the other hand may be treated as a pseudomonomolecular reaction due to the great water excess—in our reaction system 100–130 mol to 1 mol of the corresponding group. The amide group hydrolysis must be evaluated as a consecutive process with respect to the reaction of nitrile groups with water. In order to calculate the average rate constants of hydrolysis of the ester bonds the experimental data were transformed as the dependence of $\ln[B \cdot c_A/A \cdot c_B]$ on reaction time τ . In Figure 5 the dependence of ester groups hydrolysis in case of the copolymer with the middle particle size $d = 0.65$ mm at the reaction temperature 106°C is shown. The initial ratio of reacting components $A/B = 0.470$. It is evident that the course of values $\ln[B \cdot c_A/A \cdot c_B]$ can be linearized in the initial phase. This linearization was used for all the obtained values of copolymer hydrolysis. For the correlation of these results by computer processing the statistical routine for linear regression in accordance with Efronson was used.¹⁸ By this method it is possible to approximate the experimental curve by using two line segments. The first segment is a part of the straight line going from the coordinate $\ln[(B/A) \cdot (c_A/c_B)] = 0$ parallel with the time axis to τ_D which is the point of intersection of this straight

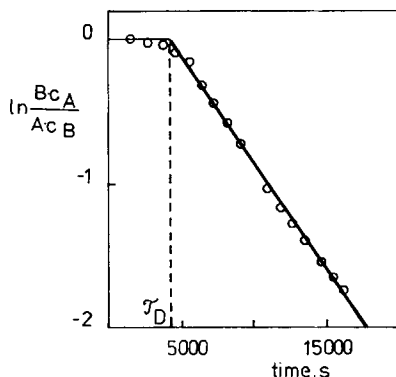


Fig. 5. Time dependence of the value $\ln [(B/A) \cdot (c_A/c_B)]$ for the middle particle size of copolymer $d = 0.65$ mm, the temperature of hydrolysis $T = 379.2$ K, and ratio of reacting components $A/B = 0.420$.

line with another one which characterizes the linear decrease of $\ln[(B/A) \cdot (c_A/c_B)]$ as the function of time. By means of this approximation the initial part is determined. In this phase the main process is diffusion of the hydrolytic agent into the particle, the point τ_D corresponds to the time when diffusion is practically finished. In further evaluations it is supposed that the value of τ_D is at least 95% of the time necessary for the total diffusion of the liquid hydrolytic agent through the copolymer particle. The gradient of the straight line the initial point of which has coordinates $(\tau_{D,0})$ is designated by m_1 . It is related to the rate constant of the proceeding reaction in accordance with the following equation:

$$m_1 = k_1 \cdot (A - B) \quad (2)$$

All the rate constants corresponding to the ester groups hydrolysis were calculated for different conditions using this equation. All their values are given in Table I.

The characteristics of nitrile group hydrolysis were evaluated using regression of values in $[N/c_N]$ as a function of time τ . From the gradient m_2 of the linear part of this relation the rate constants were calculated using following equation:

$$m_2 = k_2 \cdot H \quad (3)$$

Thus calculated values of rate constants k_2 are digested in Table I.

The rate constant k_3 for the consecutive reaction, i.e., amide groups hydrolysis was calculated from the equation

$$\tau_{\max} = \frac{1}{k_2 - k_3} \cdot \ln \frac{k_3}{k_2} \quad (4)$$

This equation results from the first-order derivative of the generally applicable equation for the time behavior of the intermediate concentration in the consecutive reaction which has in our case the following form:

$$c_{AM} = \frac{k_2 N}{k_3 - k_2} [\exp(-k_2 \tau) - \exp(-k_3 \tau)] \quad (5)$$

The condition $dc_{AM}/d\tau = 0$ leads to eq. (4). For the next calculations the value τ_{\max} was substituted for the value

$$\tau_{\max} = (\tau_{\max}^* - \tau_D) \quad (6)$$

τ_{\max}^* represents the value of the reaction time for the maximum concentration of amide groups given in Figure 4.

The values of the rate constant k_3 were evaluated by the method of step-by-step approximations on calculator HP 9100 and are given in Table I.

For the approximation of diffusion coefficients the quantity τ_D designed as "diffusion time" was used. Under above-mentioned presumptions this

TABLE I
Dependence of Rate Constants, Diffusion Time, and Diffusion Coefficient on Various Reaction Factors

K_1	k_2	k_3	τ_D	D	T	x	$2r_0$	A/B
1.688×10^{-4}	1.032×10^{-5}		3500	7.638×10^{-12}	373.2	7.8	6.5×10^{-4}	0.136
1.022×10^{-4}	9.217×10^{-6}		8900	3.004×10^{-12}	368.2	7.8	6.5×10^{-4}	0.136
8.822×10^{-5}	6.792×10^{-6}		12,800	2.088×10^{-12}	363.2	7.8	6.5×10^{-4}	0.136
5.176×10^{-5}	4.449×10^{-6}		15,700	1.703×10^{-12}	361.2	7.8	6.5×10^{-4}	0.136
2.876×10^{-5}	3.795×10^{-6}		19,500	1.371×10^{-12}	359.7	7.8	6.5×10^{-4}	0.136
6.602×10^{-6}	9.702×10^{-7}		15,000	1.782×10^{-12}	373.2	14.0	6.5×10^{-4}	0.136
6.261×10^{-5}	8.065×10^{-6}		6700	3.990×10^{-12}	373.2	11.6	6.5×10^{-4}	0.136
1.213×10^{-4}	1.290×10^{-5}		3800	7.035×10^{-12}	373.2	7.8	6.5×10^{-4}	0.136
1.617×10^{-4}	1.843×10^{-5}		2000	1.337×10^{-11}	373.2	3.9	6.5×10^{-4}	0.136
1.213×10^{-4}			11,500	8.597×10^{-12}	373.2	7.8	1.3×10^{-3}	0.136
1.142×10^{-4}			9000	8.507×10^{-12}	373.2	7.8	1.1×10^{-3}	0.136
1.213×10^{-4}			6400	8.008×10^{-12}	373.2	7.8	9.0×10^{-4}	0.136
1.213×10^{-4}			3400	7.863×10^{-12}	373.2	7.8	6.5×10^{-4}	0.136
4.421×10^{-5}	1.384×10^{-6}	2.817×10^{-4}	6000	4.455×10^{-12}	379.2	7.8	6.5×10^{-4}	0.703
1.024×10^{-4}	2.320×10^{-6}	3.595×10^{-4}	4000	6.683×10^{-12}	379.2	7.8	6.5×10^{-4}	0.470
1.533×10^{-4}	3.563×10^{-6}	6.456×10^{-4}	2500	1.069×10^{-11}	379.2	7.8	6.5×10^{-4}	0.242
1.580×10^{-4}	9.801×10^{-6}	1.104×10^{-3}	2500	1.337×10^{-11}	379.2	7.8	6.5×10^{-4}	0.186
1.812×10^{-4}	1.588×10^{-5}	2.555×10^{-3}	1700	1.573×10^{-11}	379.2	7.8	6.5×10^{-4}	0.150

quantity was used for calculation of the diffusion coefficient D using the final form of the partial differential equation integral which describes the nonsteady diffusion into the globular particle. This method is described by Jost¹³:

$$\frac{\bar{M} - M_f}{M_i - M_f} = \frac{6}{\pi^2} \cdot \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot \exp\left(\left[\frac{-n^2\pi^2 D\tau_D}{r_0^2}\right]\right) \quad (7)$$

The right side is a convergent infinite series. For the approximative evaluation, the first three members of this series were used. According to eq. (7) the approximative values of diffusion coefficients were obtained numerically (these are also presented for individual combinations of evaluated parameters in Table I.

The knowledge of rate constants k_1 and k_2 and their dependence on temperature makes it possible to calculate the apparent activation energy for hydrolysis of ester groups in copolymer to be $E_A = 126 \pm 10 \text{ kJ} \cdot \text{mol}^{-1}$ on the one hand and for hydrolysis of nitrile groups as $E_N = 83 \pm 11 \text{ kJ} \cdot \text{mol}^{-1}$ on the other. The values presented in Table I were also used for evaluation of empirical dependences of rate constants, diffusion times and diffusion coefficients on variable parameters. For the rate constant k_1 the following empirical equation was found,

$$\log k_1 = -68.4453 + 25.6242 \log(T) - 2.1680 \log(x) - 0.5697 \log(A/B) \quad (8)$$

and for the rate constant k_2 the equation;

$$\log k_2 = -55.394 + 19.763 \log(T) - 1.881 \log(x) - 1.376 \log(A/B) \quad (9)$$

The dependence of diffusion time τ_D is described by the empirical equation,

$$\log \tau_D = 121.749 - 44.398 \log(T) + 1.485 \log(x) + 1.501 \log(2r_0) + 0.613 \log(A/B) \quad (10)$$

and of diffusion coefficient D by equation,

$$\log D = -126.29 + 45.56 \log(T) - 1.49 \log(x) + 0.391 \log(2r_0) - 0.613 \log(A/B) \quad (11)$$

Statistical characteristics of these four empirical equations are presented in Table II.

CONCLUSIONS

The study presented of time dependences of the alkaline hydrolysis of ethyl acrylate-acrylonitrile-divinylbenzene copolymer beads on such factors as reaction temperature, hydrolytic agent concentration, degree of

TABLE II
Statistical Characteristics Corresponding to Eqs. (6)–(9)

Equation no.	Number of measurements	Correlation coefficient r	Critical value of the correlation coefficient $r_{0.95}$	Residual dispersion variance s^2 (for logarithmus of the value)	95% confidence interval (for the middle value)
(6)	18	0.805	0.587	6.312×10^{-3}	$\pm 18\%$
(7)	14	0.820	0.646	4.879×10^{-3}	$\pm 14\%$
(8)	18	0.912	0.628	7.185×10^{-4}	$\pm 15\%$
(9)	18	0.930	0.628	4.027×10^{-4}	$\pm 13\%$

crosslinking or copolymer particle sizes, and the following evaluation of results by using kinetic relations and empirical equations made it possible to show how the course of hydrolysis of crosslinked copolymers in the bead form is affected by these independent variable factors. The values of rate constants for hydrolysis of ester groups k_1 and nitrile groups k_2 and their dependence on investigated parameters have been evaluated. From eqs. (8) and (9) as well as from the values which are given in Table II it is evident that the confidence interval of this evaluation is below 20%. Determination of k_1 and k_2 for the temperature interval $T = 359.7\text{--}379.2$ K makes it possible to calculate the values of activation energy of proceeding reactions. It can be seen from the whole evaluation that the proceeding chemical reactions are to a great extent affected by the diffusion of a hydrolytic agent into the material of the skeleton consisting of the macromolecular substance. This influence has been quantified in eq. (10) by using the calculation of diffusion coefficients and its dependence on variable parameters. This relation is characterized by the minimum value of the residual dispersion variance from all four empirical equations. This demonstrates the fact that the calculated values of the coefficient D comply quite well with the relations of the reaction kinetics.

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APPENDIX: NOMENCLATURE

A	initial concentration of ester groups in system ($\text{mol} \cdot \text{L}^{-1}$)
a	relative absorbance
B	initial concentration of sodium hydroxide in system ($\text{mol} \cdot \text{L}^{-1}$)
c_A	ester group concentration during reaction ($\text{mol} \cdot \text{L}^{-1}$)
c_B	sodium hydroxide concentration during reaction ($\text{mol} \cdot \text{L}^{-1}$)
c_N	nitrile groups concentration during reaction ($\text{mol} \cdot \text{L}^{-1}$)
D	diffusion time ($\text{m}^2 \cdot \text{s}^{-1}$)
E_A, E_N	activation energy ($\text{kJ} \cdot \text{mol}^{-1}$)
H	initial water concentration in system ($\text{mol} \cdot \text{L}^{-1}$)
K	conversion (%)
k_1	reaction rate constant of ester groups hydrolysis ($\text{mol}^{-1} \cdot \text{s}^{-1} \cdot \text{L}$)
k_2	reaction rate constant of nitrile groups hydrolysis ($\text{mol}^{-1} \cdot \text{s}^{-1} \cdot \text{L}$)
k_3	reaction rate constant of amide groups hydrolysis ($\text{mol}^{-1} \cdot \text{s}^{-1} \cdot \text{L}$)
M	quantity of diffused sodium hydroxide; index i at the beginning, index f at the time $\tau \rightarrow \infty$, and index \bar{M} at the time τ
m	gradient (s^{-1})
N	initial concentration of nitrile groups in system ($\text{mol} \cdot \text{L}^{-1}$)
r	correlation coefficient (L)
r_0	copolymer particle radius (m)
x	content of divinylbenzene in copolymer (wt %)
s^2	residual dispersion variance (L)
T	reaction temperature (K)
τ	reaction time (s)
τ_D	diffusion time (s)

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