

## POLYMER STRUCTURE AND CATALYTIC ACTIVITY OF ION EXCHANGERS

Karel JEŘÁBEK

*Institute of Chemical Process Fundamentals,  
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát*

Received January 16th, 1980

Catalytic activity of ion exchangers prepared by partial sulphonation of styrene-divinylbenzene copolymers in reesterifications of ethyl acetate by methanol and propanol, hydrolysis of ethyl acetate and in synthesis of bisphenol A has been compared with data on polymer structure of these catalysts and with distribution of the crosslinking agent, divinylbenzene, calculated from literature data on kinetics of copolymerisation of styrene with divinylbenzene. It was found that the polymer structure of ion exchangers influences catalytic activity predominantly by changing the local concentration of acid active sites. The results obtained indicated that the effect of transport phenomena on the rate of catalytic reactions does not depend on the degree of swelling of the ion exchangers in reaction medium but it is mainly dependent on the relative affinity of reaction components to the acid groups or to the polymer skeleton.

Differences in the catalytic activity of strongly acidic organic ion exchangers are determined by differences in the structure of their polymer skeleton, since nearly all commercial types contain active sites of one kind, *i.e.* —SO<sub>3</sub>H groups attached to aromatic ring. Differences in the structure of polymer skeleton should be considered as differences in the arrangement of its polymer mass, differences in the shape being apparently of secondary importance. Even in the case of apparently porous, macroreticular ion exchangers, catalytic reaction takes place within polymer mass, since surface groups represent only small fraction of the total number of acid groups<sup>1</sup>.

For purposes of the study of relations between catalytic activity and polymer structure of organic ion exchangers, the examination of dependences of the catalytic activity of strongly acidic cation exchangers on the degree of their sulphonation turned out to be advantageous, since the process of sulphonation of these polymers depends strongly on polymer structure. Under proper conditions, sulphonic acid groups are first introduced into the most permeable parts of polymer and then sulphonation proceeds in progressively more compact parts of polymer mass<sup>2</sup>. The results of measurements of the catalytic activity of ion exchangers sulphonated to different degrees allow then to ascertain the specific activity of acid groups in different parts of polymer mass<sup>1</sup>.

The aim of this work was to find how changes in reaction medium, structure of reactants, type and rate of catalytic reaction manifest themselves in the effectiveness of active sites present in different parts of polymer mass and further how these

data, along with more detailed knowledge of the polymer structure of ion exchanger catalysts, could aid in predicting changes in the catalytic activity of ion exchangers due to changes in the structure of their polymer support. In addition to the method of partial sulphonation, we made attempt to characterize polymer structure of the ion exchangers also by calculation of the distribution of divinylbenzene used as the crosslinking agent, in the polymer mass, using reported data on kinetics of copolymerisation of styrene with divinylbenzene<sup>3</sup>. For purposes of the study of the effect of polymer structure on catalytic properties of ion exchangers we have chosen four model reactions — reesterification of ethyl acetate by methanol and by propanol, hydrolysis of ethyl acetate and the synthesis of bisphenol A from acetone and phenol. These reactions differ both in the type of reactants and in their reaction rate.

For this study we used a series of low crosslinked macroreticular poly(styrene-co-divinylbenzene). This type was chosen for the fact that its porous structure ensured a uniform distribution of sulphonic acid groups in the whole cross-section of polymer particles even for the polymers with low degree of sulphonation.

## EXPERIMENTAL

*Materials.* Phenol (Loba-Chemie) was purified by distillation, ethyl acetate, methanol, propanol and acetone (all analytical purity grade, Lachema) were dried over a molecular sieve. Ethylthiol *purum* (Fluka) and sulphuric acid (*pro analysis*, Lachema) were used without further purification.

*Polymers.* All polymers under study had low specific surface ( $< 10 \text{ m}^2/\text{g}$ ) so that its effect on catalytic activity was negligible. The polymers were prepared by Spolek pro chemickou a hutní výrobu, Ústí n/L, with nominal divinylbenzene content 10, 8, 7, 6, 4 and 3 per cent. Divinylbenzene used for their preparation was of technical grade purity and contained 18% of *p*- and 43% of *m*-isomer (the residue was ethylvinylbenzene). In all cases the polymerization was carried out at 70°C with addition of 30% of stearin as porogene.

*Sulphonation.* Besides ion exchangers sulphonated to maximal content of sulphonic acid groups, also a series of ion exchangers differing in degree of their sulphonation was used. These were prepared from the copolymer containing 10% of divinylbenzene. Sulphonation was carried out by 90% sulphuric acid without pre-swelling of the copolymer. The degree of sulphonation was controlled by reaction temperature and reaction time and was expressed as the exchange capacity of ion exchanger (*C*) which was determined by titration of the sample with 0.1N-NaOH in 0.1N-KCl; measurements of concentration gradients of sulphur by electron microprobe made on samples of the particles of all the partially sulphonated ion exchangers grounded into a plane passing through the grain, centre proved satisfactory homogeneity of the sulphonation in the whole cross-section of particles (deviations max.  $\pm 20\%$  of the average value).

Temperature, °C	25	40	40	50	60	90
Time, h	4	5	6	3	3	3
<i>C</i> , meq./g	0.124	0.233	0.591	1.10	1.60	5.03

*Apparatus and procedure.* Catalytic activity of ion exchanger catalysts was tested by measuring initial reaction rates of model reactions in an ideally mixed flow glass microreactor ( $6\text{ cm}^3$  volume), which was similar to that used by Rodriguez and Setínek<sup>4</sup>. The weighed amount of catalyst was 0.05–0.2 g and flow rate of the reaction mixture was changed from 10 to  $40\text{ cm}^3/\text{h}$ . Samples of reaction products were removed after  $20\text{ cm}^3$  of the reaction mixture had passed through the reactor. This volume was found to be sufficient for establishing steady state conditions. Reaction conditions used in experiments were chosen so that conversions did not exceed 10%; in this case the reaction rates were independent of conversion. Initial reaction rates of the synthesis of bisphenol A were determined at  $70^\circ\text{C}$  and the phenol : acetone molar ratio = 8 : 1. In agreement with recommendation reported in patent literature<sup>5</sup>, 0.5 w.% of ethylthiol was added to the reaction mixture. Reaction products were analysed by high performance liquid chromatography, using  $4.1\text{ m} \times 250\text{ mm}$  column filled with Nucleosil  $\text{C}_{18}$  (Marcherey-Nagel Co.), using methanol–water mixture (66 : 34) as the mobile phase. Detection was made spectrophotometrically at 290 nm that ensured very suitable ratio of detector response to phenol and bisphenol A. Further three reactions were performed at  $53^\circ\text{C}$ . Reaction rates of reesterification of ethyl acetate by propanol and methanol were measured for equimolar concentrations of both components, those of hydrolysis of ethyl acetate by using this compound in 6 w.% concentration in water. Reaction products obtained by the above reactions were analysed by gas chromatography at  $225^\circ\text{C}$  on 3 m long column packed with Porapak Q (Waters Assoc.). The resulting value of catalytic activity determined for each catalyst studied was the average of at least 3, typically 5–7 measurements.

## RESULTS AND DISCUSSION

Dependence of catalytic activity on sulphonation degree was studied only for the copolymer with nominal divinylbenzene content 10% (Fig. 1). In order to calculate the catalytic activity of sulphonic acid groups introduced into the polymer in different stages of sulphonation process, it was necessary to determine what portion

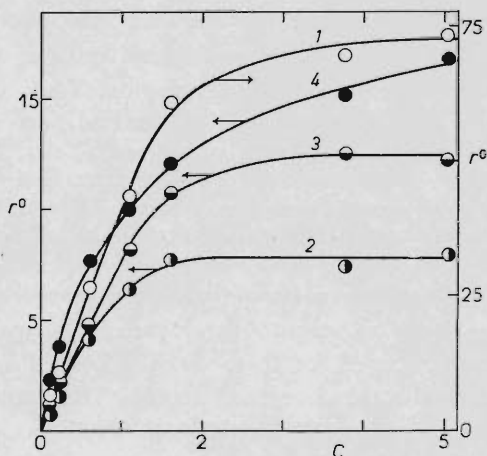


FIG. 1

Dependence of initial reaction rates  $r^0$  (mmol/h g) on exchange capacity  $C$  (mmol/g) of partially sulphonated ion exchangers prepared from copolymer with nominal divinylbenzene content 10%. 1 Reesterification of ethyl acetate by methanol, 2 reesterification of ethyl acetate by propanol, 3 hydrolysis of ethyl acetate, 2 synthesis of bisphenol A

of the sulphonated polymer mass corresponds to the exchange capacities of individual ion exchangers. The calculation was made by taking into account the difference in the mass of polymer unit of the sulphonated and unsulphonated part of the polymer by using relation (1) in which  $P$  is per cent of sulphonated polymer mass,

$$P = 100C / \{ C + [(1000 - M_s C) / M_p] \}, \quad (1)$$

$C$  is the exchange capacity of ion exchanger in meq/g,  $M_s$  and  $M_p$  are medium molecular weights of sulphonated and unsulphonated monomer unit of the polymer, respectively (for the polymers under study these values were as follows:  $M_s = 188.6$  and  $M_p = 108.5$ ). Providing that each ion exchanger sulphonated to the greater exchange capacity has sulphonic acid groups located in the same parts as the ion exchanger with the nearest lower exchange capacity and other set of active acidic sites is then introduced into part of polymer mass of the lower permeability, six different degrees of sulphonation define six sets of active sites introduced into six fractions of the polymer mass which differ in their permeability. Percentual proportion of these fractions in the polymer mass of the copolymer with nominal divinylbenzene content 10%, calculated according to Eq. (1), is presented in Table I (the sum of percentual proportion of all fractions is not equal to 100%, since the highest exchange capacity attained, *i.e.* 5.03 meq/g corresponds to sulphonation of only 92% of the polymer mass).

Absolute values of initial reaction rates of individual model reactions differed considerably from one another. It was therefore convenient to express catalytic activities of differently sulphonated ion exchangers as the relative values of their effectiveness,  $\eta_c$ , which were calculated from initial reaction rates related to the unit of exchange capacity ( $r_s^0$ ). For this purpose the average  $r_s^0$  values calculated from data for the most active (least sulphonated) samples were taken as the basis (100%), since their  $r^0$  values did not differ by more than 10%. The effectiveness of acidic active sites in individual fractions of the polymer mass was then calculated from these data by differentiation. Thus, for example, the effectiveness of active sites present in the last sulphonated part of the polymer mass,  $\eta_{(1.60-5.03)}$ , was calculated from Eq. (2) where  $\eta_{5.03}$  and  $\eta_{1.60}$  are the

$$\eta_{(1.60-5.03)} = (\eta_{5.03} \cdot P_{5.03} - \eta_{1.60} \cdot P_{1.60}) / (P_{5.03} - P_{1.60}) \quad (2)$$

relative effectiveness of the ion exchangers sulphonated to the capacity 5.03 and 1.60 mequiv./g, resp.,  $P_{5.03}$  and  $P_{1.60}$  are per cent of the sulphonated polymer mass obtained for these catalysts according to Eq. (1). A similar calculation was made also for the other fractions. The results are presented in Table I. It is evident that for all model reactions, the high specific activity was exhibited only by small portion of sulphonic acid groups introduced into the polymer in the very beginning

of the sulphonation process. The activity of the acid groups introduced in further stages of sulphonation to increasingly more rigid parts of the polymer decreased significantly. The most pronounced decrease in specific catalytic activity with increasing exchange capacity was observed for the synthesis of bisphenol A. In other three reactions difference in the mode of the action of polymer structure was substantially less distinct.

In characterizing polymer structure of the ion exchanger catalysts with lower crosslinking we assumed that relative proportions of individual fractions of the polymer mass can be determined by calculation based on the so far reported data on kinetics of copolymerisation of styrene with divinylbenzene. Excellent survey of these data has been published by Schwachula<sup>3</sup> who also showed how important is the molar ratio of *meta* to *para* isomer in divinylbenzene used as the crosslinking agent. Copolymerisation of styrene with divinyl benzene should be therefore regarded as three component system. The basic relation used in this calculation was the equation derived by Alfrey and Goldfinger<sup>6</sup>. It described dependence of the molar ratio of individual components incorporated into the copolymer on molar ratio of these components in a mixture of monomers. Numerical values of the constants expressing the relative reactivity of styrene, *m*- and *p*-divinylbenzene were taken from Schwachula<sup>3</sup>. Ethylvinylbenzene was not included in calculation, since its concentration in the reaction mixture was always very low (max. 4%). The above relation was used to calculate changes in proportion of crosslinking components in the course of polymerization for different starting nominal divinylbenzene concentrations ( $[B]_0$ ). The calculation involved only the reaction of first vinyl group, *i.e.* its incorpo-

TABLE I

Relative catalytic activity of acid active groups ( $\eta$ ) present in individual fractions of polymer mass of cation exchanger of poly(styrene-co-divinylbenzene) type with nominal divinylbenzene content 10%. *C* Exchange capacity, *P* portion of sulphonated mass, indices at  $\eta$  designate type of reaction: a reesterification of ethyl acetate by methanol, b reesterification of ethyl acetate by propanol, c hydrolysis of ethyl acetate, d synthesis of bisphenol A

<i>C</i> meq/g	<i>P</i> %	$\eta_a$	$\eta_b$	$\eta_c$	$\eta_d$
		%			
0—0.124	1.4	100	100	100	100
0.124—0.223	1.1	100	100	100	74
0.223—0.591	4.3	81	100	79	56
0.591—1.10	6.3	65	62	72	26
1.10 —1.60	6.9	68	41	71	25
1.60 —5.03	72.0	16	9	13	10



ration into polymer chain and no assumptions concerning the reactivity of the second vinyl group of divinylbenzene have been made. The results relate therefore only to distribution of the crosslinking agent and not to distribution of the formed crosslinking bonds. Nevertheless, these data can serve well for characterization of distribution of permeability for a series of the polymers prepared under similar conditions. Examples of calculated dependences are shown in Fig. 2 and demonstrate considerable heterogeneity of crosslinking agent distribution. The permeability of polymer skeleton depends not only on the content of crosslinking agent but also on mutual entanglement of polymer chains which is influenced by reaction medium used in copolymerization<sup>7</sup>. The so calculated distribution of crosslinking agent characterizes only changes in polymer structure of a series of copolymers prepared with the use of the same porogene. In the case of polymers under study this assumption is fully justified. Let us assume that sulphonation proceeds progressively from the most permeable parts of the polymer (characterized by the lowest content of crosslinking agent) to the parts with increasing content of crosslinking agent. For fractions of the polymer mass, differentiated by the method of partial sulphonation in the copolymer

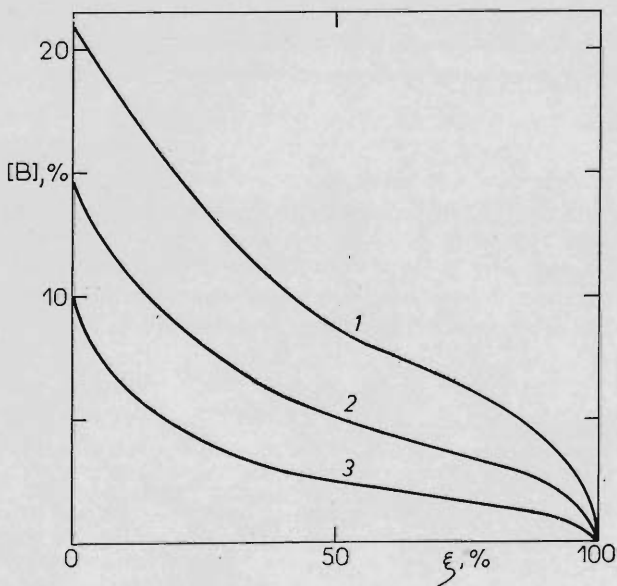


FIG. 2

Calculated dependences of actual content of divinylbenzene in copolymer ( $[B]$ ) on conversion of monomers ( $\xi$ )  $[B]_0$ : 1 10%, 2 6%, 3 3%

with  $[B]_0 = 10\%$  (characterized by exchange capacity  $C$ ), one can determine the corresponding region of divinylbenzene concentration ( $[B]_{\text{calc}}$ ) from the calculated crosslinking agent concentration; similar calculations for the other copolymers with different  $[B]_0$  allowed to determine (Table II) theoretical relative proportion of individual fractions in these copolymers ( $q$  with index corresponding to  $[B]_0$ ).

These data and relative catalytic activities of acid groups presented in Table II were used to calculate theoretical dependences of the catalytic activity of tested ion exchanger catalysts on the nominal content of divinylbenzene in basic polymer skeleton for each model reaction studied. Comparison of these calculated dependences with experimental data is shown in Fig. 3. Very good agreement between theoretical and experimental data has been found for all three reactions carried out in nonaqueous medium (both reesterifications) or in medium containing water in low concentration (the synthesis of bisphenol A where water is one of reaction products). This shows that the catalytic effectiveness of individual fractions measured with the use of the ion exchanger with  $[B]_0 = 10\%$  is valid obviously generally for these fractions, even though their relative proportion in the polymer mass changed significantly due to the decrease in  $[B]_0$ . This fact is clearly demonstrated for the most permeable fractions of the polymer mass. While the relative content of first two fractions of the polymer (corresponding to divinylbenzene content 0–2.14%) form 2.4% of the polymer mass in the ion exchanger with  $[B]_0 = 10\%$ , in the case of the ion exchanger with  $[B]_0 = 3\%$  they represent already 42% of the polymer mass. The structure of macroreticular copolymers can be considered as being formed by clusters of micro-

TABLE II

Calculated values of relative proportion of individual fractions of polymer mass ( $q$ ) of poly(styrene-co-divinylbenzene) with different nominal divinylbenzene content ( $[B]_0$ , value as index at  $q$ ). Fraction of copolymer with  $[B]_0 = 10\%$ :  $C$  exchange capacity,  $[B]_{\text{calc}}$  calculated divinylbenzene content

$C$ mequiv./g	$[B]_{\text{calc}}$ %	$q_3$	$q_4$	$q_6$	$q_7$	$q_8$
		%				
0—0.124	0—0.8	9	5	2	2	1
0.124—0.223	0.8—2.1	33	18	7	5	4
0.223—0.591	2.1—3.4	27	30	15	10	7
0.591—1.10	3.4—4.6	11	16	20	15	11
1.10—1.60	4.6—5.7	8	9	14	16	14
1.60—5.03	5.7	12	22	42	52	63

balls, the surface layer of which consists of the most permeable parts of the polymer mass. The thickness of this layer and thus also diffusion path of the reacting molecules increases from 0.9% to 17% of the particle radius on going from the ion exchanger with  $[B]_0 = 10\%$  to that with  $[B]_0 = 3\%$ , *i.e.* by more than eighteen times. Despite of this fact, for three model reactions experimental data agree well with the predicted increase in the catalytic activity with decreasing  $[B]_0$  from 10% to 3%. This indicates that for these reactions transport phenomena, which should depend on the length of diffusion path, do not exert important effect. On the other hand, in the case of hydrolysis of ethyl acetate, the catalytic activity of ion exchanger catalysts increases with decreasing  $[B]_0$  at substantially slower rate than is predicted by calculation. The catalytic effectiveness of acid groups in individual fractions of the polymers with low nominal divinylbenzene content is therefore markedly lower than that found by the method of partial sulphonation of the copolymer with  $[B]_0 = 10\%$ . In this case, increasing diffusion path plays likely a role and the rate of hydrolysis of ethyl acetate is affected by transport phenomena.

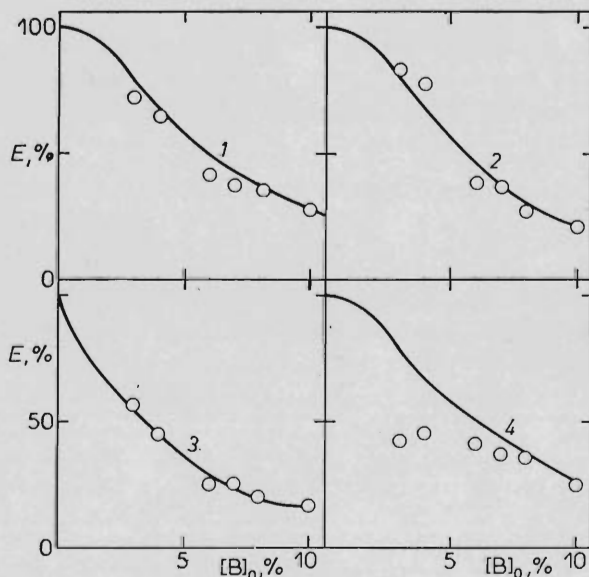


FIG. 3

Comparison of calculated and experimental dependences of activities of ion exchanger catalysts ( $E$ ) on nominal divinylbenzene content ( $[B]_0$ ). Reactions: 1 reesterification of ethyl acetate by methanol, 2 reesterification of ethyl acetate by propanol, 3 synthesis of bisphenol A, 4 hydrolysis of ethyl acetate



This finding is at variance with widely accepted concept about the effect of swelling on the course of transport processes in ion exchangers. Swelling of ion exchangers in water is substantially greater than in organic solvents, *e.g.* in ethyl acetate; measurements carried out at room temperature by reported procedure<sup>11</sup> with samples having  $[B]_0 = 4, 6$  and 10% led to the following data (water/ethyl acetate, in per cent of the volume of the dry sample): 440/197, 240/157, 194/141. The increased swelling of ion exchanger catalyst cannot be connected directly to the increased ease of transport processes. In the swelled polymer gel, the mechanism of transport of reactant molecules is not analogous to diffusion in liquid volume phase, since the swelled gel cannot be considered as the system of pores filled with liquid. Each molecule in the swelled gel phase interacts either with acid active group or with polymer skeleton. Transport of reactant molecules is therefore mediated only *via* this interaction for which diffusing molecules must compete one to another. If reacting molecules differ much in their affinity to the gel of ion exchanger catalysts, which is the case of water and ethyl acetate, transport of ethyl acetate molecules through polymer gel can be so difficult that it retards the rate of catalytic reaction.

By contrast to this, good agreement between calculated and experimental dependences of catalytic activity on nominal divinylbenzene content for the above reesterifications and the synthesis of bisphenol A show that in these cases the catalytic activity of individual fractions of the polymer mass is not influenced by increasing diffusion path. Also rather small difference in the effectiveness of individual fractions for reesterifications of ethyl acetate by methanol and propanol (Table I) speaks for rather weak effect of transport phenomena, although reaction rates of these two reactions differ by nearly one order of magnitude (Fig. 1). Nevertheless, also in these reactions the specific activity of acid groups depends (in the synthesis of bisphenol A even very strongly) on the structure of the polymer mass into which these groups were introduced. This can likely be explained in terms of the effect of the polymer structure on the local configuration of sulphonic acid groups. If a certain arrangement of two or more active sites is a prerequisite for the course of catalytic reaction<sup>8,9</sup>, then the probability of formation of such an arrangement due to the tendency of sulphonic acid groups to associate *via* hydrogen bonding is greater for more flexible, less crosslinked fractions of polymer mass than for the more rigid, higher crosslinked fractions. This effect can be compared with the effect of the local concentration of active groups. Therefore, the sensitivity of different reactions to the change of the structure of ion exchanger catalysts should be similar to their sensitivity to changes in the concentration of acid groups achieved by different way. In order to verify this hypothesis, we have prepared samples of catalysts from the ion exchanger with  $[B]_0 = 3\%$ , the acid group concentration of which was adjusted by neutralisation to 80, 60 and 40% of the initial value. In Fig. 3 are plotted experimental relative values of catalytic activities for both reesterifications and for the synthesis of bisphenol A (related to the activity of the starting ion exchanger) in loga-

rhythmic coordinates against the concentration of active groups expressed as per cent of the sulphonic acid groups present in acid form (not neutralised). From Fig. 4 it is seen that in the coordinates used, the dependence of catalytic activity on the concentration of active sites is nearly linear, although similarity in deviations of experimental points from the straight line indicates that such a correlation is only approximative. The slope of correlation lines calculated by linear regression equals to 2.94 for reesterification of ethyl acetate by methanol, to 4.06 for reesterification of ethyl acetate by propanol and to 10.22 for the synthesis of bisphenol A. These data cannot be surely interpreted simply as the number of active sites which participate in the rate determining step. However, they can be taken as characterizing demands of a given reaction for a certain configuration of active sites for which the probability of its occurrence depends on the local concentration of acid groups. For the fractions of polymer mass corresponding to the range of exchange capacity 0.591–1.6 mequiv./g in the ion exchanger with  $[B]_0 = 10\%$ , and in the case of the synthesis of bisphenol A, the relative activity was found to be 25–26% (Table I). From data in Fig. 3 it becomes apparent that the same decrease in the reaction rate which was realized in a series of partially sulphonated cation exchangers by the change in their polymer structure, can also be attained by the decrease in acid group concentration due to neutralization to 87% of the initial value. In the case of reesterification of ethyl acetate by methanol the same concentration decrease led to the decrease in reaction rate to 67% and in reesterification of ethyl acetate by propanol to 57 per cent. These data comport well with data about the average activity of the mentioned fractions of polymer mass (corresponding to 0.591–1.6 mequiv./g exchange capacity region) for re-

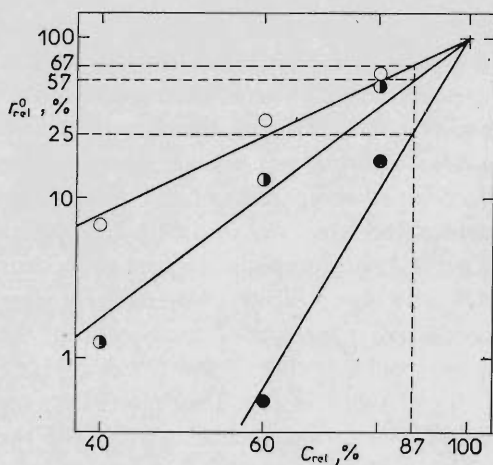


FIG. 4

Dependence of relative initial reaction rates  $r_{rel}^0$  on relative exchange capacity  $C_{rel}$  of ion exchanger catalyst with nominal divinylbenzene content 3%. Reactions: ○ reesterification of ethyl acetate by methanol, ◐ reesterification of ethyl acetate by propanol, ● synthesis of bisphenol A

esterification reactions, *i.e.* 66.5% for the reaction with methanol and 51.5% (average values) for the reaction with propanol (Table I). The effect of structure of polymer mass on the rate of studied model reactions corresponds to changes in the concentration of acid active groups.

*The author thanks Mr J. Šrejber, Spolchemie Ústí n/L, for basic polymer skeletons and Mrs J. Aunická, this Institute, for experimental assistance.*

#### REFERENCES

1. Jeřábek K.: This Journal 44, 2612 (1979).
2. Jeřábek K.: J. Polym. Sci., Polym. Chem. Ed. 18, 65 (1980).
3. Schwachula G.: J. Polym. Sci., Symp. Ser. 53, 107 (1975).
4. Rodriguez O., Setínek K.: J. Catal. 39, 449 (1975).
5. Farnham A. G., Bender H. L. (Union Carbide Corp.): Fr. 1, 513 814 (1968).
6. Alfrey T., Goldfinger G.: J. Chem. Phys. 12, 322 (1944).
7. Millar J. R., Smith D. G., Marr W. E., Kressman T. R. E.: J. Chem. Soc. 1963, 218.
8. Thornton R., Gates B. C.: J. Catal. 34, 275 (1974).
9. Jeřábek K., Bažant V., Beránek L., Setínek K.: *Proc. Vth Int. Congr. Catal., Miami Beach* 1972, p. 1193. North Holland Publ. Co., Amsterdam 1972.
10. Zundel G.: *Hydration and Intermolecular Interaction. Infrared Investigations with Polyelectrolyte Membranes*. Academic Press, New York 1969.
11. Setínek K.: Chem. Prům. 26, 535 (1976).

Translated by J. Hetflejš.