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Reactions

Phase Transfer Catalysis

2. The Reaction Between Phenol and n-Butyl Bromide Catalyzed with Polyethyleneglycols Fixed on Macroporous Glycidylmethacrylate Copolymers

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Summary

By using a model reaction between sodium phenoxide and n-butyl bromide, the PTC activity of a number of polyethyleneglycols (PEG) fixed on the macroporous glycidyl methacrylate copolymer (0.09 - 0.7 mmol PEG/g) was tested and compared with that of dissolved polyethyleneglycols. Both systems are catalytically active; 1 mmole of fixed PEG raises the reactivity 168 times, and in solution 139 times compared with the uncatalyzed reaction. In the case of immobilization, PEG 2000 and higher are catalytically somewhat more active than in solution; the lower activity of immobilized PEG´s with mol.wt up to 1550 is interpreted by the lower mobility of parts of the chain due to immobilization. The rise in catalytic activity with the molecular mass of fixed PEG is in accord with their higher sorption ability towards cations of alkali metals.

Introduction

Polyethyleneglycols are potential phase transfer catalysts (PTC). Their relatively low price and low toxicity make them more advantageous compared with crowns. In the case of reactions catalyzed with PEG, it was the effect of the chain length of polyethyleneglycols on catalytic activity that was investigated in the first place; as a rule, the activity increases with the chain length and does not change to any considerable extent starting from PEG 2000. With respect to their catalytic activity, polyethyleneglycols can be compared with crowns (BANTHIA et al., 1981), where the salt transfer mechanism is similar. It seems that at low temperatures polyethyleneglycols are more active (HRADIL and ŠVEC, 1983), although here the main role is of course played by the character of the reaction. By joining crowns to PEG with M.W. 300-14 000, no rise in the PTC activity was achieved (HARRIS et al., 1982), while after the binding of cryptands the activity somewhat increased. Three-block copolymers polystyrene-polyethyleneglycol are very active as PTC (KELLY et al., 1979, 1982).

After the immobilization of PEG on silicagel, the activity was the same as with free coronands (SAVICKY, 1982). The activity of polyethyleneglycol ether bound to the styrene-divinylbenzene copolymer (REGEN and DULAK, 1977) is also high.

In our paper, we have compared the activity of polyethyleneglycols immobilized on the macroporous copolymer glycidylmethacrylate - ethylenedimethacrylate with that of nonimmobilized polyethyleneglycols.

Experimental

Investigation of the reaction kinetics

2 mmoles of sodium phenoxide, 0.26 g of dry sorbent (polyethyleneglycol immobilized on the macroporous glycidylmethacrylate copolymer),[x)] 2 ml water (in the case of soluble polyethyleneglycols, 2 ml of a solution of 0.5 g PEG in 10 ml H_2O) and 2 ml of the solution of 0.3491 g (2.548 mmole) of n-butyl bromide in toluene (1:6) were introduced into a stirred reactor, 5 ml in volume. The reactor was heated to 50°C ± 0.03°C and stirred with a propeller stirrer (1300 r.p.m.). From the reaction mixture, two samples of the organic phase were taken in 30 min. intervals and analyzed immediately by gas chromatography on a column 1 m long and packed with Chromosorb N-AW-DMCS with 10% of the deposited PEG 1550 (grain size 0.16 - 0.20) at 90°C. The concentrations of n-butyl bromide were calculated from two measurements of samples and calibration standards with toluene as the internal standard, relative error being ± 1.0%.

Assuming a first-order reaction rate (HARRIS et al., 1982), the rate constants k_1 (s^{-1}), rate constants related to 1 mole of PTC, k_1' (s^{-1} $mmole^{-1}$), relative rate constants for PEG immobilized against free PEG, k_{rel}, and relative rate constants for 1 mmole PEG related to the uncatalyzed reaction, k_{rel}' ($mmol^{-1}$), were calculated.

Chemicals

Polyethyleneglycols 200, 400, 600, 1550, 2000 and 4000 pract. (SERVA, Feinbiochemica, Heidelberg). G-60-PEG 200, 400, 600, 1550, 2000 and 4000 prepared by a reaction between sodium polyethyleneglycol (NaH + PEG) and the macroporous copolymer glycidylmethacrylate - ethylenedimethacrylate (40 wt.% crosslinking agent, S_g 55.5 m^2/g, V_g 1.47 ml/g, porosity 65%) in dioxan (100°C, 12 h). These sorbents were characterized by the content of PEG groups estimated from the elemental analysis of carbon, sorption of KCl, content of carboxylic groups and porosity in water.

Results and Discussion

Characteristics of immobilized polyethyleneglycols

By reacting the macroporous glycidylmethacrylate copolymer crosslinked with 40 wt.% of ethylenedimethacrylate with sodium salts of several polyethyleneglycols having molecular weights between 200 and 4000, a number of derivatives containing 0.1 - 0.7 mmole PEG/g carrier were prepared (Table I). The content of PEG introduced into the carrier decreases systematically with the molecular weight of PEG. This finding may be explained by carrying out the reaction under equilibrium conditions of the stirred reactor, and thus by employing the lower mobility of PEG with higher molecular weights during the diffusion in beads of the macroporous copolymer. Another factor is

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x) The authors are indebted to Dr J. Kahovec for kind supply of the sample; its preparation and properties will be reported by the same author in a separate paper.

Table I. Properties of macroporous glycidyl methacrylate copolymers with immobilized polyethyleneglycols

Copolymer	Content of groups, mmol/g		Sorption of 0.1 mol/l KCl				Water regain	Porosity
	PEG[a]	COOH[b]	Dynamically[c] mmol/g	P,%[d]	Statically[e] mmol/g	P,%[d]	g H_2O/g	%
G-60-PEG 200	0.7	2.7	0.045	6.4	0.097	13.8	2.12	73
G-60-PEG 400	0.5	2.1	0.170	32.1	0.084	15.8	1.90	71
G-60-PEG 600	0.8	1.8	0.125	55.3	0.060	7.9	1.90	71
G-60-PEG 1550	0.1	1.1	0.094	78.3	0.059	49.2	1.55	67
G-60-PEG 2000	0.1	1.2	0.125	125	0.128	128	1.88	71
G-60-PEG 4000	0.1	2.4	0.018	20.0	0.110	122	2.02	72

[a] Content of PEG groups bound on the glycidyl methacrylate copolymer according to the elemental carbon content.

[b] Resin transformed by 1 mol/l HCl into the H-form; the content of COOH group determined after eluting 0.1 mol/l NaOH and washing with ethanol, by retitration of the eleunt.

[c] Sorbent washed with 1 mol/l HCl, distilled water, 5 ml of 0.1 mol/l KCl added dropwise, during 5 minutes, eluent retitrated argentometrically.

[d] Ratio of the sorbed amount of KCl to the total content of PEG groups according to a).

[e] Sorbent shaken at 25°C for 66 h with 0.1 mol/l KCl, determined as sub c).

the finding that the surface accessible to the low-molecular weight PEG is much larger than for the higher-molecular weight ones, even if the porous structure makes possible penetration of both types, because according to GPC the upper exclusion limit for PEG is 10^5. The reactivity of macroporous copolymers is always proportional to the average molecular weight of the agent (HORÁK et al., 1983).

Along with polyethylene glycol groups, the polymers contain also carboxylic groups (1.0-2.7 mmol/g) which act as sorbents with respect to alkali metals hydroxides (Table I), but are not operative as catalysts in the system under investigation. It was found that, under the given conditions, Lewatit CNP 80 containing 4.5 mmol of COOH groups/ml is catalytically inactive ($k_1 = 1.38 \times 10^{-6} s^{-1}$). This means that there is neither any considerable reaction between carboxylate and n-butyl bromide with formation of ester, as such reaction requires a higher temperature and water is not the best medium, nor any substitution reaction accompanied by the formation of alcohol.

Copolymers with immobilized polyethyleneglycol groups are capable of sorption also from aqueous KCl solutions in an amount up to 0.128 mmol/g, as follows from sorption in dynamic and static conditions. The amount of sorbed KCl increases with increasing molecular weight of polyethyleneglycols, although the molar content of anchored PEG (obtained on the basis of elemental analysis) decreases in the same series. The KCL PEG ratio in this series increases, and for PEG 2000 reached the highest value. The sorption of KCl cannot be attributed to carboxylic groups, because their acidity is low and they are therefore not able to split a neutral salt.

In water, porosity of the sorbents does not change too much irrespective of modification (p = 70% ± 3%), but is higher compared to the starting copolymer.

PTC activity of polyethyleneglycols

The PTC activity of fixed polyethyleneglycols was examined using the reaction between sodium phenoxide and n-butyl bromide in the water-toluene system. The rate constants thus determined (k_1, s^{-1}) are incomparable for the particular catalysts, owing to the different content of fixed PEG. The comparable standardized values of the rate constants related to 1 mmole PEG increase with the molecular weight of PEG, even though the content of fixed groups decreases in the same series. This suggests the higher selectivity of bound PEG groups with a higher molecular weight which ensues from their higher sorption capacity towards alkali metals (Table II), compared with lower-molecular weight homologs. The highest sorption values of KCl and the strongest effect of PTC were found for the copolymer with immobilized PEG 2000.

The catalytic effect of soluble PEG on the reaction under investigation is weaker, but the dependence of the rate constant, k_1, on the molar weight of PEG in the system is similar to that of PEG fixed on the macroporous copolymer; the highest activity can be observed for PEG 1550. Both catalytic systems are illustrated in Fig.1. The shift of the highest rate constant value from soluble PEG 1550 to immobilized PEG 2000

Table II. Kinetics of alkylation of phenol in presence of PEG as PTC

Conditions: 0.2300 g sodium phenoxide, 0.26 g G-60-PEG, 2 ml H_2O (or 2 ml of solution of 0.5 g PEG in 10 ml H_2O), 2 ml of n-butyl bromide mixture in toluene (1:6), 50°C.

PTC	Amount of PEG in reaction mmol	First-order rate constant		Relative rate constant	
		k_1, s^{-1} x 10^6	k_1', $s^{-1} mmol^{-1}$ x 10^6	with respect to PEG k_{rel}	with respect to noncatal. k_{rel}', $mmol^{-1}$
G-60-PEG-200	0.181	4.80	26.5	-	20
G-60-PEG-400	0.138	1.56	11.3	-	9
G-60-PEG-600	0.198	5.50	27.8	1.68	21
G-60-PEG-1550	0.031	3.12	101	0.56	78
G-60-PEG-2000	0.026	5.56	214	2.75	168
G-60-PEG-4000	0.024	3.27	131	1.64	105
PEG-600	0.169	2.97	17.6	1.0	14
PEG-1550	0.064	11.5	180	1.0	139
PEG-2000	0.050	3.93	78.6	1.0	61
PEG-4000	0.025	2.07	82.8	1.0	64
Without PTC	-	1.29	-	-	-

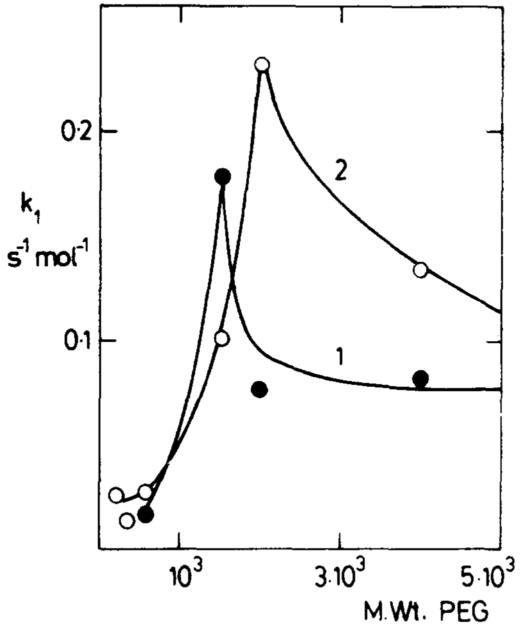

Fig.1 Rate constant (k_1 s^{-1} mol^{-1}) of the alkylation of phenol with n-butyl bromide catalyzed with polyethylene glycols: soluble (curve 1, ●) and immobilized on glycidylmethacrylate macroporous copolymers (curve 2, ○)

can be interpreted by the lower mobility of the fixed part of the chain, even though the chain has been extended due to the immobilization reaction.

By comparing the catalytic effect of polyethyleneglycols with the uncatalyzed reaction, one can see that 1 mmole of PEG 1550 raises the rate constant 139 times, while 1 mmole of bound PEG 2000 raises the same constant 168 times. The catalytic activity of these systems is stronger than in the case of crowns; another advantage is their easier preparation.

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