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Poly(styrene)s with oligo(ethylene oxide) side chains as catalysts for phase transfer reactions

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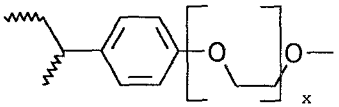
Summary

A very interesting part within the wide field of chemical reactions are catalyzed reactions. To find an effective low cost catalyst for various applications is a primary goal of many workers. Polymer chemistry is able to provide systems with qualities not known for monomeric catalysts. Especially in heterogenic systems the use of polymeric catalysts has many advantages such as easy separation for reuse or low toxicity. A special type of heterogenic catalysis is the phase transfer catalysis. Comb polymers of poly(styrene) with oligo(ethylene oxide) side chains were investigated for their ability as phase transfer catalysts.

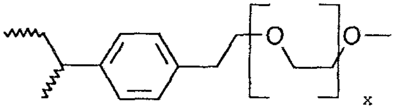
Introduction

In a two phase system, as for example water/toluene, one hydrophilic educt can be brought to the other in the organic phase by a carrier. Much work has been done for such systems using various polymers (1-4). A special group were polymers with poly(oxyethylene) structures in the main or side chain, examples of which are oligo(oxyethylene) substituted poly(styrene) comblike polymers.



1

	x
a	2
b	3
c	4



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The compounds investigated in this work were poly(p-1,4,7-trioxooctane-styrene ether) **1a**, poly(p-1,4,7,10-tetraoxoundecane-styrene ether) **1b** and poly(p-1,4,7,10,13-pentaoxotetradecane-styrene ether) **1c** in which the oxygen atom of the oligo(ethylene oxide) side chain is directly connected with the phenyl ring of the main chain poly(styrene), and a second series with ethylene spacered oligo(ethylene oxide) side chain comprising compounds **2a-2c**. As a well known test reaction the hydrolysis of 1-bromadamantane (5) was chosen (Figure 1).

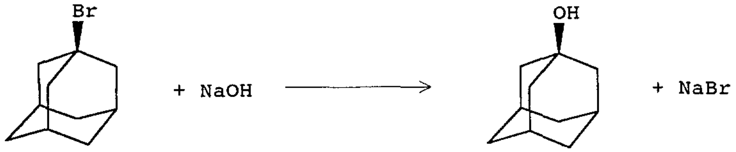

Figure 1: Hydrolysis of 1-bromadamantane

A common disadvantage in the investigations of reaction rates is their dependence of the geometry of the reactor and the stirring rate. An attempt was made to use 18-crown-6 as a standard to make all data comparable.

Experimental part

Monomer preparation and polymerization

All monomers were prepared and polymerized as described earlier (6).

Phase transfer activity

10 mL of 1 N aqueous NaOH and 10 mL 1-bromadamantane in toluene (0.1 mol/L) were placed in a 50 mL round flask. The mixture was stirred and heated to a constant temperature. 1 mL of a toluenic polymer solution (0.01 mol/L) was added. After certain periods of time 0.1 mL of the aqueous phase was mixed with 2 mL of an aqueous $KMnO_4$ solution (ca. 0.002 mol/L). The decrease of $KMnO_4$ is proportional to Br^- formed during the reaction and can be determined very easily by UV measurements.

Temperature controlled solubility

The temperature controlled solubility was measured by DSC.

Instrumentation

A Rheometric Science DSC-Gold differential scanning calorimeter was used to measure the glass transition temperature. The Tg was taken at the midpoint of the baseline shift. UV/Vis-Spektrophotometer PERKIN-ELMER Lambda 5 was used for UV measurements.

Results and discussion

An Arrhenius plot of the reaction rates for the hydrolysis of 1-bromadamantane by various polymers **1a-2c** gives the activation energy which shows a significant dependence on the side chain length of the polymers, see Figure 2. As the side chain is responsible for the hydrophilicity of the polymer the solubility in water increases dramatically with the side chain length. The temperature controlled solubility is a good indicator for the hydrophilicity of a polymer (Table 1). An increasing solubility of the catalyst in water allows a better interaction between the two separated phases (7).

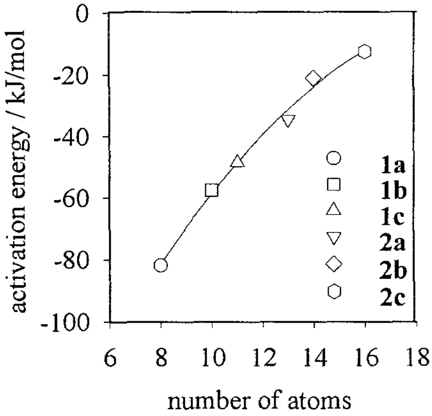

Figure 2: Activation energy for the 1-bromadamantane hydrolysis reaction influenced by polymers **1a**-**2c**

Table 1: Critical solution temperature for an aqueous polymer solution (c = 1 mg/mL)

Polymer	Critical solution temperature / °C
1a	<<0
1b	-2,0
1c	14,0
2a	2,5
2b	21,5
2c	40,5

A great disadvantage of all measurements of catalytic activity of a system is their dependence on the geometry of the reactor and the stirring rate. Both factors alter the area of the contact surface which is essential for the reaction to proceed. To make data comparable we suggest to use a gauging standard. The crown ether 18-crown-6 is a readily available substance with phase transfer catalytic activity. The achieved data can be related to the data of 18-crown-6 in order to make them comparable (Figure 3). A phase transfer reaction can be catalyzed in two different ways (8). The polymer is able to transport one reaction partner from one phase into another, or it forms a new phase at the contact surface (Figure 4). In the cosolvent mechanism the third phase is a real solution of the two solvents stabilised by the polymer, while in the surface-area mechanism the solvents form a microphasic mixture thus increasing the contact surface. In both cases the reaction rate increases. A possible way to determine the type of the catalytic reaction is the comparison of the free Gibbs energy. In opposite to the surface-area mechanism the energy for the cosolvent mechanism is constant for all temperatures. The free Gibbs energy can be calculated with the theory of the activated complex.

$$\Delta G^{0\neq} = -RT \cdot \ln K^{\neq} \text{ with } K^{\neq} = \frac{h}{kT} \mathrm{k}_n$$

k_n represents the reaction constant for one temperature. The results are shown in Figure 5.

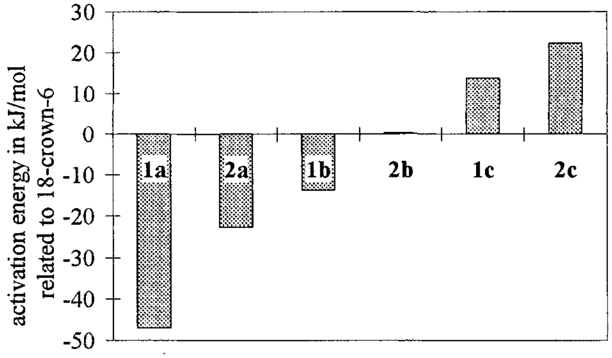

Figure 3: Activation energy of the polymers related to 18-crown-6

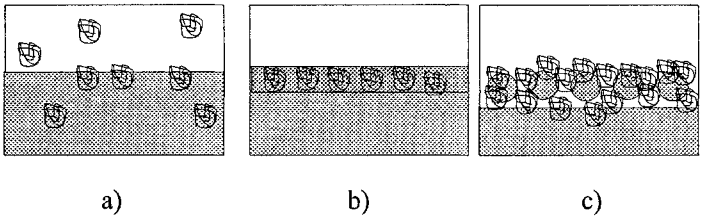

Figure 4: Possible mechanisms for a heterogenic two phase reaction:

a) The catalyst is mainly in the contact surface
b) The catalyst forms a third phase (cosolvent mechanism)
c) The catalyst forms a microphasic mixture (surface-area mechanism)

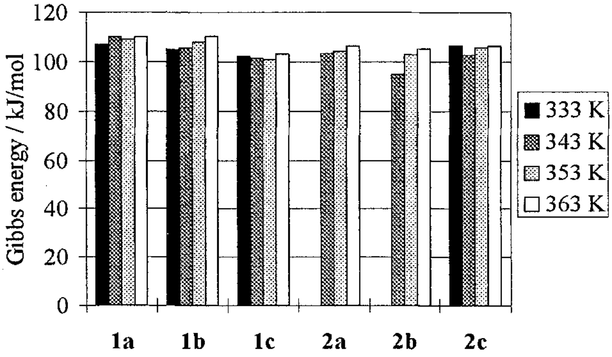

Figure 5: Free Gibbs energy

The Gibbs energy can be regarded as constant which indicates a cosolvent mechanism.

Conclusions

Polymers with poly(ethylene oxide) structures in the side chain are phase transfer catalysts. With their ballanced hydrophilicity/hydrophobicity they are able to form a new phase at the contact surface in which both solvents are soluble. Within this phase the reaction takes place (cosolvent mechanism). To make data independent of the surrounding we suggest to use 18-crown-6 as a gauging standard.

Acknowledgement

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