Crosslinked poly(ethylene oxide) as a phase transfer catalyst

T. Tsanov, R. Stamenova* and C. Tsvetanov

Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

(Received 3 December 1991; revised 7 May 1992)

The gel of radiation crosslinked poly(ethylene oxide) (PEO) was used as a highly active phase transfer catalyst in the model displacement reaction of 1-bromooctane with aqueous sodium and potassium cyanides in the absence of organic solvent. The reaction follows pseudo-first-order kinetics and the rate is linearly dependent on the amount of PEO gel. The reaction rate is not limited by intraparticle diffusion and mass transfer at stirring speeds above 200 rev min^{-1}. Crosslinked PEO is easily produced in large quantities from commercially available polymer so it may be used successfully as a gel medium for phase transfer catalysis in various substitution reactions.

(Keywords: crosslinking; poly(ethylene oxide); catalyst)

INTRODUCTION

Polymer-supported macrocylic polyethers (crown ethers and cryptands) and linear polyethers have considerable advantages as phase transfer catalysts in various reactions taking place in liquid–liquid and liquid–solid phases. The catalysts form a third phase that can be easily separated by filtration and reused or they can be used in flow systems such as packed and fluidized bed reactions. Polyethylene glycols bound to inert inorganic or organic supports are known as active catalysts in nucleophilic reactions such as substitution and redox processes being comparable to crown ethers[1]. Immobilization of polyethers without an inert polymer support can be realized by irradiation crosslinking of high-molecular-weight poly(ethylene oxide) (PEO). The most interesting feature of the PEO gel is the ability to swell in water and in organic solvents which enables the uniform distribution on a microscopic level of the water and organic phase inside the gel particles providing a high specific interfacial area and fast mass transfer. The PEO gel obtained via irradiation has a low crosslinking density[2]; $\bar{M}_c$ varying from 5000 to 2000 with increase in irradiation dose from 1 to 10 Mrad. The gel swells well in water and in many organic reagents such as halogen-containing solvents and substrates. Under such conditions, diffusion limitation on the intrinsic reactivity is eliminated and the catalytic activity of the gel can be comparable or better than that of the soluble polyether.

The availability of PEO and the simple crosslinking method are good reasons to study the catalytic properties of the gel. This is why the liquid–liquid substitution reaction of 1-bromooctane with sodium cyanide in the absence of organic solvent was investigated. This reaction is frequently used in studies of the mechanism of classical phase transfer catalysts: ammonium and phosphonium quaternary salts[3,4] as well as cyclic and linear polyethers[5,6]. Swollen gel used in a stoichiometric quantity with respect to the substrate was used as the reaction medium. This type of polymeric catalyst is often termed a polymeric cosolvent.

EXPERIMENTAL

Materials. 1-Bromooctane, toluene, n-dodecane, sodium cyanide, potassium cyanide and linear PEO ($M_w = 20\,000$) were purchased from Fluka AG and were used without further purification. 1-Cyanooctane was distilled under reduced pressure. Degassed 2 wt% aqueous solutions of high-molecular-weight PEO (BADIMOL™, Bulgaria), $M_v = 2.5 \times 10^6$, were irradiated with γ rays from a ^{60}Co source (intensity 270 krad h^{-1}). The gels formed were washed three times with distilled water and freeze dried. Gels obtained via irradiation with 2, 5 and 10 Mrad doses were used. Different sized particles (10, 100 and 1000 μm) were obtained by grinding in liquid nitrogen and sieving.

Displacement reaction of 1-bromooctane with sodium cyanide. A 10 ml thermostatically controlled glass reactor was charged with catalyst and 5 M NaCN (3 ml, 15 mmol) and left for 20 min at room temperature to condition the catalyst. The reaction mixture was heated to the chosen temperature and 1-bromooctane (0.386 g, 2 mmol) was added. The mixture was stirred with a magnetic stirrer for a certain period of time and then cooled and toluene (2 ml) containing n-dodecane as internal standard was added. The mixture was vigorously stirred for 5 min. Then the organic phase was separated and analysed by g.l.c. (Carlo Erba, model Fractovap 4100 with a capillary column). The continuous process was carried out in a thermostatically controlled glass column (12 cm^3 effective volume) connected to a flow system as described in reference 7. 1-Bromooctane and aqueous sodium cyanide solutions were premixed to form an emulsion which was pumped to the column. The reaction product was collected in tubes containing toluene (2 ml) and n-dodecane as an internal standard.

---

*To whom correspondence should be addressed

0032-3861/93/030616-05

© 1993 Butterworth-Heinemann Ltd.

Kinetics. Each run consisted of five samples taken over periods ranging from 20 to 100 min. No deviation from the pseudo-first-order was observed.

Swelling of the catalyst. Dry PEO gel was weighed into a tared column with a fritted bottom[8]. It was then soaked at room temperature for 48 h in the solvent. The excess liquid was removed by centrifugation for 10 min at × 1100 *g* and the swollen gel was then weighed.

Imbibed solvent composition. The general procedure used for determining the imbibed solvent composition was as follows. A glass column with a fritted bottom was weighed together with dry crosslinked PEO (44 mg, 1 mmol). After adding 5 M NaCN (3 ml, 15 mmol) and 1-bromooctane (0.345 ml, 2 mmol; 0.356 ml, 2 mmol 1-cyanooctane) the mixture was left to stand for 20 min and then shaken for 1 h. After filtering for 30 s under reduced pressure the column with the swollen gel was weighed to obtain the total amount of imbibed constituents (D). The reproducibility of D was $\pm 5\%$. Toluene (5 ml) with n-dodecane was added to the filtrate and two phases were separated. The aqueous phase was diluted up to 100 ml and an aliquot of the resulting solution (25 ml) was titrated with 0.1 N $AgNO_3$. The weight of sodium cyanide (B) was then calculated. The amount of 1-bromooctane or 1-cyanooctane (A) in the toluene layer was measured by g.l.c. The amount of adsorbed water was calculated from the relationship: $C = D - B - A$.

RESULTS AND DISCUSSION

Rate measurements

Reaction rates were measured by using a large excess of aqueous sodium cyanide (usually 7.5 mol per mol n-$C_8H_{17}Br$). In order to present the rate data a mechanism was assumed similar to that suggested elsewhere[9]. Oxyethylene chains swollen in aqueous sodium cyanide and 1-bromooctane interact with the alkali cation to form an anion activated complex which, having been transferred into the halide phase, reacts with it forming 1-cyanooctane. If the amount of the complex is constant during the reaction, the conversion will be a pseudo-first-order process:

$$\text{rate} = K_{\text{obs.}}\,[\text{substrate}] \qquad (1)$$

The observed rate constant, $K_{\text{obs.}}$, depends linearly on the quantity of catalyst (*Figure 1*).

Effect of stirring speed

The rate constant increased rapidly with the stirring speed up to 200 rev min^{-1}, after which the increase was slight (*Figure 2*). Mass transfer from the liquid phase to the surface of the catalyst particles was attained at 200–300 rev min^{-1}; above this speed it was no longer a limiting factor. Without stirring, $K_{\text{obs.}}$ was 0.26×10^{-5} s^{-1} at a molar ratio of substrate to catalyst of 1:1.5.

Effect of catalyst particle size and crosslinking density

Tables 1 and *2* report the dependence of $K_{\text{obs.}}$ on catalyst particle size and on crosslinking density, respectively. The reaction rate does not depend on the particle size and the degree of crosslinking. The PEO gel has a loose network, permeable for the reagents. Thus the whole system could be considered as analogous to phase transfer catalysis with homogeneous catalyst dissolved in both liquid phases.

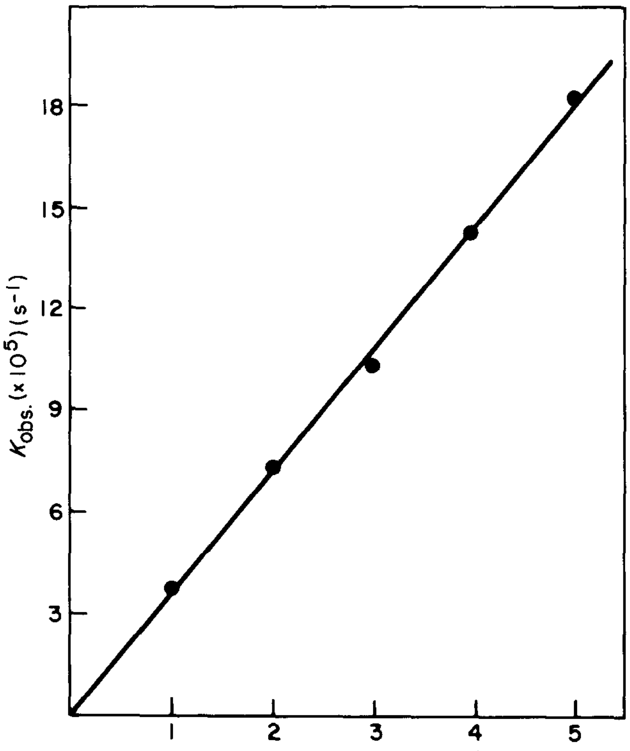

Figure 1 Dependence of $K_{\text{obs.}}$ on the amount of crosslinked PEO in the reaction of 1-bromooctane (2 mmol) with sodium cyanide (15 mmol) in water (3 ml) at 90°C

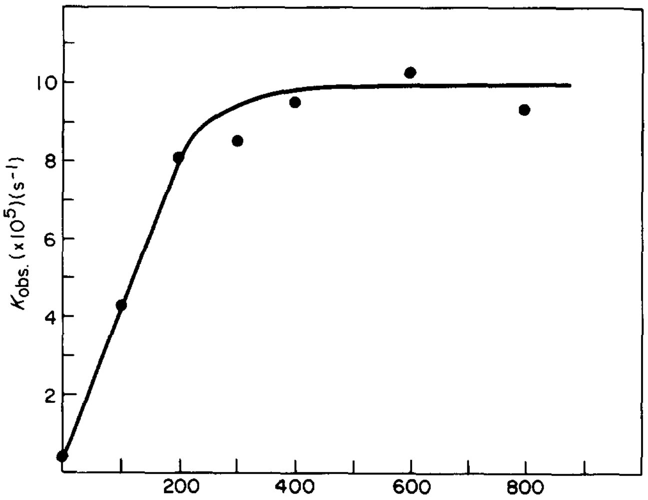

Figure 2 Dependence of $K_{\text{obs.}}$ on the stirring rate: $C_8H_{17}Br$ (2 mmol); 5 M NaCN (3 ml); crosslinked PEO (3 mmol, 2 Mrad); 90°C

Table 1 Dependence of $K_{\text{obs.}}$ on the catalyst particle size[a]

Mean particle size (μm)	$K_{\text{obs.}}$ (× 10^5) (s^{-1})
1–10	8.80
90–120	8.35
1000–2000	7.35

[a] $C_8H_{17}Br$ (2 mmol), 5 M NaCN (3 ml, 15 mmol), crosslinked PEO (2 mmol, 2 Mrad); 90°C; 600 rev min^{-1}

Table 2 Dependence of $K_{obs.}$ on crosslinking density[a]

Total dose (Mrad)	$\bar{M}_c$ (mol g^{-1})[b]	$K_{obs.}$ (× 10^5) (s^{-1})
2	4700	10.28
5	3900	9.80
10	2600	10.47

[a] $C_8H_{17}Br$ (2 mmol), 5 M NaCN (3 ml, 15 mmol), crosslinked PEO (3 mmol, 2 Mrad); 90°C; 600 rev min^{-1}

Effect of sodium cyanide concentration

Catalytic activity is proportional to the quantity of inorganic salt in the aqueous phase (*Figure 3*). A three-fold increase in catalyst in the reaction mixture gives a six times faster rate due to the increased complexation constant. An important reason for this effect is the reduced hydration of the reactant anions because of the growing deficiency of water molecules. *Table 3* shows the drastic decrease in the degree of swelling with increasing sodium cyanide concentration, but this does not limit the reaction rate. The effect is the reverse when an additional amount of sodium bromide, the salt formed by the leaving group, is added instead of sodium cyanide. $K_{obs.}$ decreases twice when 15 mmol sodium bromide is added to 15 mmol sodium cyanide owing to the blocking of the active sites of the polyether chains.

Effect of temperature

The linear log $K_{obs.}$ *versus* $1/T$ plot of the reaction in the temperature interval 60–105°C (*Figure 4*) yields the activation parameters of the reaction with both sodium and potassium cyanides (*Table 4*). Above 90°C the slope drastically dropped down and the rate constant remained almost constant for the temperature increase from 90 to 105°C. Above this temperature the reaction became diffusion controlled. PEO is known to be insoluble above 90°C[10]. Gel particles shrink and the intraparticle diffusion of the aqueous phase is inhibited. In the range 60–95°C rather high values for the activation energy were obtained. The entropy change has a positive sign.

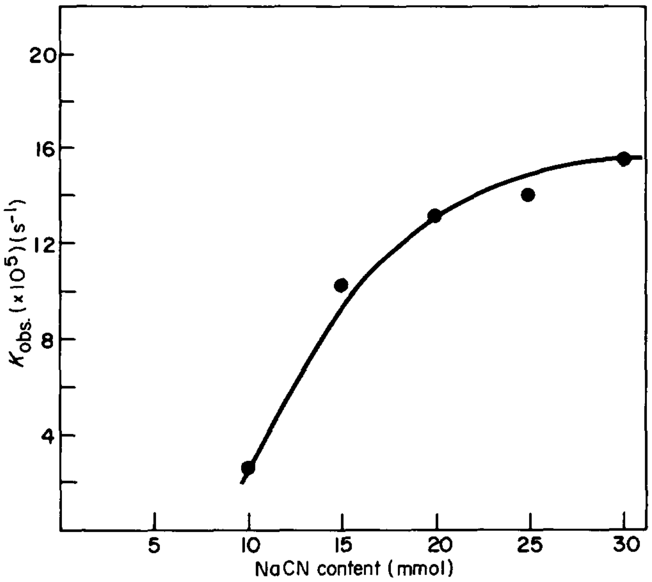

Figure 3 Dependence of $K_{obs.}$ on sodium cyanide concentration: $C_8H_{17}Br$ (2 mmol); crosslinked PEO (3 mmol, 2 Mrad); 90°C; 600 rev min^{-1}

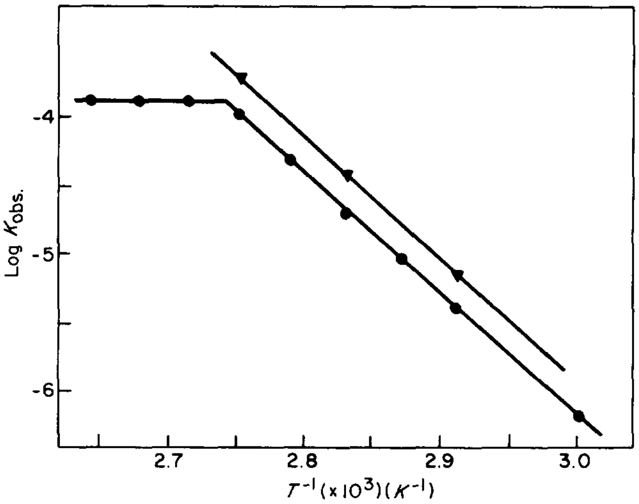

Figure 4 Apparent activation energy plot for the reaction of 1-bromooctane with sodium (●) and potassium (▼) cyanides. Conditions as in *Figure 2*

Table 4 Apparent activation energy (E_{app}) and change in entropy ($\Delta S^{\neq}$) for the reaction of 1-bromooctane with sodium and potassium cyanides[a]

Nucleophile	E_{app} (kcal mol^{-1})	$\Delta S^{\neq}$ (e.u.)[b]
NaCN	40.5	32.4
KCN	40.9	34.8

[a] Conditions as in *Figure 2*
[b] At 90°C

Phase composition of the gel medium

On the basis of the swelling procedures of Ohtani *et al.*[11] a simple method for analysing imbibed solvent composition under three-phase conditions has been developed. A given weight of dry gel is equilibrated with an appropriate amount of mixture of the aqueous solution and organic reagent followed by rapid suction filtration. A definite amount of toluene with n-dodecane is added to the filtrate. The analysis of organic (g.l.c.) and aqueous (titration) portions of the filtrate yields the weight of imbibed 1-bromooctane or 1-cyanooctane (*A*) and sodium cyanide (*B*), respectively. The added weight

Table 3 Dependence of the degree of swelling and $K_{obs.}$ on sodium cyanide concentration in the aqueous solution

NaCN concentration (mol l^{-1})	0	1	2	3	4	5	6.66	8.33
Degree of swelling	28.5	24.5	21.8	18.8	14.3	8.2	3.5	2.8
$K_{obs.}$ (× 10^5) (s^{-1})[a]					5.8	10.3	12.8	14.0

[a] Crosslinked PEO (3 mmol, 2 Mrad); other conditions as in *Figure 2*

of the gel (*D*) represents the sum of the imbibed consftituents. The weight of adsorbed water (*C*) is obtained from the relationship: $C = D - A - B$. *Table 5* summarizes the data obtained.

Under two-phase conditions, crosslinked PEO is extensively swollen by water and moderately swollen by 1-bromooctane or 1-cyanooctane. Under three-phase conditions, the amount of imbibed water remains unchanged but there is a substantial increase in bromooctane uptake. Dissolving sodium cyanide in the aqueous phase caused a strong reduction in adsorbed water. When subjected to three-phase conditions, the imbibed water content was further reduced almost twice whereas the amount of imbibed bromooctane is greater than in the case for two-phase conditions, the sodium cyanide concentration being essentially unchanged. Obviously, crosslinked PEO exhibits great osmotic and catalytic response to changes in the salt concentration of the exterior aqueous phase.

Reuse of PEO gel catalyst

The crosslinked PEO was reused five times and almost no change in the rate constant of the reaction was observed (*Table 6*). This proves that the stability is sufficiently high to ensure long-term use. Carrying out the reaction as a continuous process the substrate and the aqueous sodium cyanide solution were premixed and pumped through a column, containing crosslinked PEO (60 mmol) at a speed of 15 ml h^{-1} without stirring. After ~6 h equilibrium was established in the system and the conversion reached 31–33%.

For comparison, the observed rate constant ($K_{obs.}$) of the reaction with homogeneous catalyst (linear PEO, $M_v = 20000$) was determined (*Table 7*). $K_{obs.}$ with crosslinked PEO as a catalyst is a little higher than the value for the reaction with linear PEO at a stirring speed eliminating the effect of mass transfer as a limiting factor.

Regen *et al.* studied the catalytic activity of polyethylene glycols grafted upon gel-type crosslinked polystyrene in the liquid–liquid substitution reaction of 1-bromooctane with sodium cyanide in toluene without stirring[12]. Using a ratio of 5 mol% ethylene oxide ligands with respect to the substrate no activity was observed. The same reaction has been studied in the presence of polymer-supported ammonium and phosphonium phase transfer catalysts in various solvents and it has been found that their activity drastically increases when the organic solvent is eliminated from the reaction mixture[13]. It is known that the catalytic activity of polymer-supported phase transfer catalysts or polymeric cosolvents is determined by two major factors: the quantity of the extracted inorganic salt and its intrinsic reactivity[14]. Obviously, the amount of inorganic salt extracted by crosslinked PEO into the alkyl halide provides sufficient concentration of ion pairs for the reaction to proceed (*Table 5*). For the liquid–liquid cyanide displacement reaction neither crown ethers nor linear polyethers are sufficiently effective. The nucleophile CN^- is a small 'hard' anion, the activity of which is diminished by the strong hydrogen binding of water molecules. Crosslinked PEO is hydrophilic and is of a lower activity compared to crown ethers. This is confirmed by the high activation energy of the reaction (*Table 4*). On the other hand, the positive change in entropy shows that hydrate water is released from the structure of the transition state favouring the formation of a 'softer' intermediate. The rate of displacement of 1-bromooctane with sodium cyanide in PEO gel medium is independent of the size of catalyst particles and network density. This shows that the intraparticle diffusion of the substrate and the reagent are not rate limiting factors. The first order of the reaction in catalyst is an indication that a constant amount of PEO salt complex is rapidly formed relative to the rate of conversion of 1-bromooctane into cyanide. Crosslinked PEO differs from the known polymer cosolvents mainly by its higher swelling capacity both in water and in the substrate. Being in an amount comparable to that of the substrate, the swollen gel plays the role of an immobile medium, where the reaction proceeds. The optimal conditions for carrying out the displacement reaction of 1-bromooctane with sodium cyanide should be elimination of the organic solvent and use of stoichiometric amounts of PEO gel. Crosslinked PEO is easily produced in large quantities so it is convenient to use as the gel medium for phase transfer catalysis of various substitution reactions.

Table 5 Amount of imbibed reagents (g g^{-1}) in PEO gel under two- and three-phase conditions at room temperature

Swelling conditions	NaCN	H_2O	n-$C_8H_{17}Br$	n-$C_8H_{17}CN$
Water	–	27.5	–	–
n-$C_8H_{17}Br$	–	–	1.8	–
n-$C_8H_{17}CN$	–	–	–	1.2
Water/n-$C_8H_{17}Br$	–	30.2	5.3	–
5 M NaCN	3.7	9.1	–	–
5 M NaCN/n-$C_8H_{17}Br$	3.4	4.6	2.4	–
5 M NaCN/n-$C_8H_{17}CN$	2.9	4.9	–	1.6

Table 6 Reuse of catalyst in the reaction[a]

Run no.	$K_{obs.}$ ($\times 10^5$) (s^{-1})
1	11.2
2[b]	11.3
3	11.6
4	11.0
5	10.5

[a] Conditions as in *Figure 2*

[b] Catalyst recovered by washing alternately with alcohol and water, and drying

Table 7 Comparison of crosslinked PEO with linear PEO as reaction catalysts[a]

Catalyst	$K_{obs.}$ ($\times 10^5$) (s^{-1})
PEO ($M_v = 20000$)	7.6 (at 200 rev min^{-1})
Crosslinked PEO (2 Mrad)	10.3 (at 600 rev min^{-1})

[a] Conditions as in *Figure 2*

ACKNOWLEDGEMENT

The authors would like to acknowledge the financial support of the National Foundation for Scientific Research, Sofia, Bulgaria (Project X-30).

REFERENCES

1 Tomoi, M. and Ford, W. T. 'Syntheses and Separations using Functional Polymers' (Eds D. C. Sherrington and P. Hodge), J. Wiley & Sons, Chichester, 1988, p. 182

2 Minkova, L., Stamenova, R., Tsvetanov, C. and Nedkov, E. *J. Polym. Sci., Polym. Phys. Edn* 1989, **27**, 621

3 Regen, S. L. *Angew. Chem., Int. Edn Engl.* 1979, **18**, 421

4 Tomoi, M. and Ford, W. T. *J. Am. Chem. Soc.* 1981, **103**, 3821

5 Quici, S. and Regen, S. L. *J. Org. Chem.* 1980, **45**, 1700

6 Fukunshi, K., Bronislaw, C. and Regen, S. L. *J. Org. Chem.* 1981, **46**, 1218

7 Stamenova, R. T., Tsvetanov, C. B., Vassilev, K. G., Tanielyan, S. K. and Ivanov, S. K. *J. Appl. Polym. Sci.* 1991, **42**, 87

8 Stamberg, J., Sevcik, S. *Collect. Czech. Chem. Commun.* 1966, **31**, 1009

9 Wakui, T., Xu, W. Y., Chen, Ch.-S. and Smid, J. *Makromol. Chem.* 1986, **187**, 533

10 Bailey, F. E. and Koleske, J. V. 'Poly(ethylene oxide)', Academic Press, New York, 1976, pp. 31–33

11 Ohtani, N., Wilkie, C. A., Nigam, A. and Regen, S. L. *Macromolecules* 1981, **14**, 516

12 Regen, S. L., Heh, J. C. K. and McLick, J. *J. Org. Chem.* 1979, **44**, 1961

13 Chiles, M. S., Jackson, D. D. and Reeves, P. C. *J. Org. Chem.* 1980, **45**, 2915

14 Ford, W. T. and Tomoi, M. *Adv. Polym. Sci.* 1984, **55**, 49