Triphase catalysis of a nucleophilic substitution reaction by cross-linked polycations prepared from 4-vinylpyridine and α,ω-dibromoalkanes

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Introduction

Triphase catalysis has been attracting increasing attention since the pioneering work of Regen[1,2]. The greatest advantage of this catalysis over phase transfer catalysis lies in the fact that the catalyst can, in principle, be recovered by simple filtration and used repeatedly. Various types of catalysts have been developed for triphase catalyses, including ammonium salts, phosphonium salts, crown ethers and cryptands, anchored to either insoluble polymers or surface functionalized inorganic supports and even alumina[2,3]. However, the mechanism of triphase catalysis still remains ambiguous[2]. The use of catalysts of well-defined structure is believed to be one of the prerequisites to establish this mechanism.

From this viewpoint, the spontaneous polymerization of vinylpyridines upon quaternization with α, ω-dihalides is particularly interesting in that it permits one-pot synthesis of a variety of crosslinked polymers of controlled structure without difficulty. Nevertheless, such cross-linked polymers had been used only as ion-exchange resins[4] and not as catalysts until we recently applied them to heterogeneous catalyses[5-7]. Here, we report the triphase catalytic efficiency of the crosslinked polycations prepared from 4-vinylpyridine and α, ω-dibromoalkanes for a nucleophilic substitution reaction in relation to their structure.

Results and discussion

The bulk polymerization of 4-vinylpyridine upon quaternization with an α, ω-dibromoalkane, $Br(CH_2)_x Br$, in a molar ratio of 2:1 proceeded at a moderate rate at 25°C. *Figure 1* shows the yield of the methanol-insoluble crosslinked polymer and the methanol-soluble polymer after 7 days, as a function of the length of $(CH_2)_x$ in the dibromide. Here, the yield is defined as wt% of the product in comparison with the theoretical yield for the formation of an ideally crosslinked polymer consisting only of unit structure I (see *Figure 2*). The yield of the crosslinked polymer increased with increasing x, reaching the maximum at an x value of about 5 and then decreasing gradually with increase in x. The yield of the methanol-soluble polymer was extremely low except for that at x = 2 where the crosslinking reaction is less likely to occur because of lower reactivity of 1, 2-dibromoethane compared with that of higher homologues (see below)[8].

The main unit structures of the crosslinked polymer are I–IV (*Figure 2*), of which I, III and IV have the same elemental composition. Elemental analyses of the cross-linked polymers obtained indicated that the monoquaternized unit structure, II, was formed in all cases, particularly when lower homologues of the dibromides were

used. It has been suggested[5,9] that the rate-determining step of the spontaneous polymerization is the quaternization step. Therefore, the content of the diquaternized unit structure having a pendant vinyl group, III, would not (if at all) be very high. The formation of IV will be much less likely than that of I and of some significance only when the length of $(CH_2)_x$ is suitable for loop formation. Thus, based on the assumptions that the crosslinked polymer does not contain III and IV and that the difference between 100% and the total percentage content of C, H, N and Br is due to the oxygen of the water absorbed on the sample during the isolation procedure, the molar ratio of II to I can be estimated approximately from the elemental analyses data.
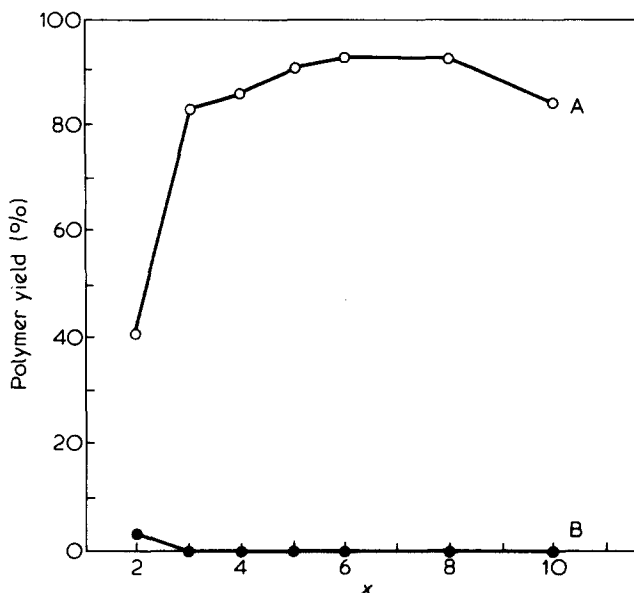

Figure 1 Bulk polymerization of 4-vinylpyridine upon quaternization with α,ω-dibromoalkanes. Yields: A, the methanol-insoluble cross-linked polymer (—○—); and B, the methanol-soluble polymer (—●—) *versus* the length of $(CH_2)_x$ in the dibromides. (For the reaction conditions, see Experimental)

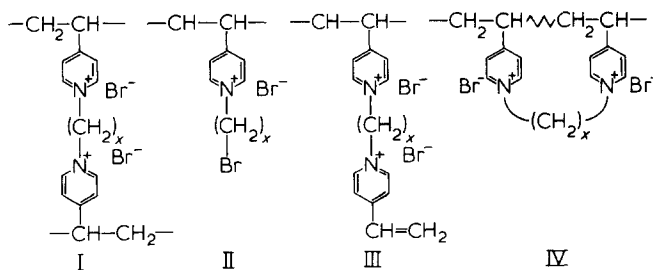*Figure 2* Unit structures of the crosslinked polycation prepared from 4-vinylpyridine and α,ω-dibromoalkane

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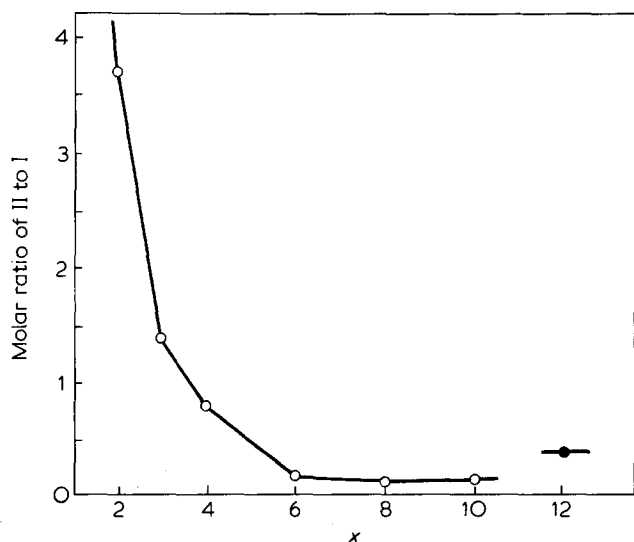* To whom correspondence should be addressed.

Figure 3 Variation of the molar ratio of II to I in the crosslinked polymers prepared by bulk polymerization (—O—) and solution polymerization (—●—) as a function of the length of $(CH_2)_x$ in α,ω-dibromoalkanes

Figure 3 shows the results of such calculations for bulk polymerization ($x = 2$–10) and solution polymerization in N, N-dimethylformamide ($x = 12$). The molar ratio of II to I is exceptionally high at $x = 2$, reflecting the low reactivity of 1, 2-dibromoethane in a substitution reaction[8]. It should be noted that, at $x = 2$, II predominates over I and hence the degree of crosslinking or the rigidity of the polymer network is smaller, and also the organophilicity of the polymer is larger than expected for the ideally-crosslinked polymer consisting of unit structure I only.

Figure 4 shows the triphase catalytic efficiency of the crosslinked polymers for the nucleophilic substitution reaction of n-octyl bromide with cyanide ion at 70°C as a function of the length of $(CH_2)_x$ in the dibromide. The yield of n-octyl cyanide increased, in general, with increase in x but was higher at $x = 2$ than at $x = 3$, yielding a minimum catalytic activity at $x = 3$.

Interpretation of the appearance of the minimum catalytic activity is possible in terms of, for example: (i) the organophilicity of the catalyst; or (ii) the flexibility or the pore size of the polymer network. These two features naturally increase with increasing x, and are unusually high at low x values due to the high content of unit structure II (see above). Thus, both (i) and (ii) are expected to be minimum at certain values of x. On the other hand, an increase in the organophilicity of the catalyst has been observed to favour an increased catalytic activity in triphase catalyses as well as in phase transfer catalyses[2,10,11]. Similarly, an increase in the pore size of the polymer network evidently favours the access of the substrate to the catalytic sites located inside the catalyst particles and hence an increase in their catalytic activity. Thus, it is now tentatively but reasonably shown that the triphase catalytic efficiency is minimum at $x = 3$.

The simplicity of the synthesis of the present catalysts compared with that of the previous ones[2,12,13] no doubt constitutes the greatest merit in their use. However, in some cases they decomposed to a certain extent under the conditions applied to the triphase catalysis. For all that, the general profile of the catalytic efficiency with a minimum at $x = 3$ (*Figure 4*) is believed to reflect the effect of the polymer structure (*Figure 3*) on the catalytic activtiy.

A more detailed study is currently underway to evaluate further crosslinked polycations of the present type as heterogeneous catalysts.

Experimental

Synthesis of Crosslinked Polycations. 4-Vinylpyridine (20 mmol) was allowed to react with an α,ω-dibromoalkane (10 mmol) in the dark for 7 days at 25°C. The reaction proceeded at a moderate rate to afford eventually an extremely hard mass. After it was triturated in methanol, the methanol-insoluble crosslinked polymer was filtered and washed thoroughly with methanol. After drying to a constant weight at 55°C–60°C under high vacuum, it was obtained in the form of an orange–yellow powder. The filtrate was concentrated to ~ 2 ml below 25°C. Then, a large volume (>200 ml) of acetone was added with stirring to the residual solution. The precipitate formed, i.e. the methanol-soluble polymer, was filtered, washed with acetone and dried as above. The results are summarized in *Figure 1*.

With 1,12-dibromododecane, 20 ml of N,N-dimethylformamide was used as solvent and the reaction was carried out for 14 days. The products were isolated as before. The yields of the methanol-insoluble and the methanol-soluble polymer were 88.1 and 1.3%, respectively.

Triphase catalysis by the crosslinked polycations

A suspension of a crosslinked polymer (0.5 mmol ammonium groups) in a mixture of n-octyl bromide (10 mmol) and ethyl benzene (1.0 ml as an internal standard for g.l.c. analysis) was gently stirred for 2 h at room temperature, using a Teflon-coated magnetic bar. Sodium cyanide (30 mmol) and distilled water (2.0 ml) were then added to the system. The resulting mixture was allowed to react at 70°C with stirring at a speed of ~ 900 rpm. The yields of n-octyl cyanide after 24 and 48 h were estimated by means of g.l.c.
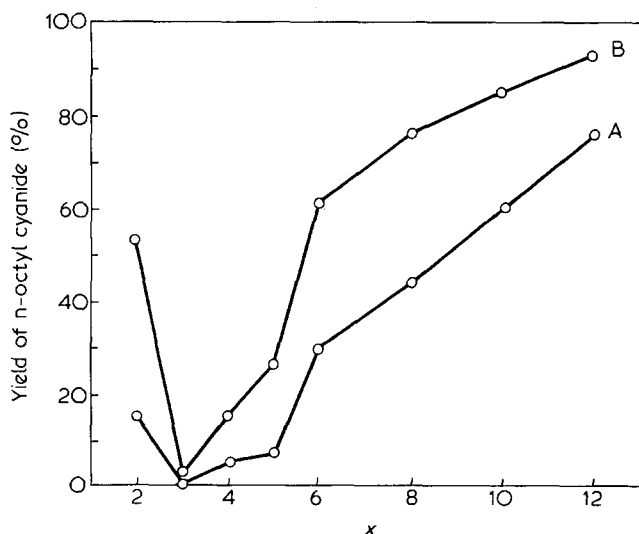

Figure 4 Triphase catalytic efficiency of the crosslinked polymers in the nucleophilic substitution reaction of n-octyl bromide with cyanide ion. Yields of n-octyl cyanide after: A, 24 h; and B, 48 h, as a function of the length of $(CH_2)_x$ in α,ω-dibromoalkanes. (For the reaction conditions, see Experimental)

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Water-treeing as an osmotic phenomenon

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Introduction

In a recent paper, Meyer and Filippini[1] discussed the propagation mechanism of water-treeing, which is described as a fracture phenomenon caused by mechanical stresses of electrical origin, observed in the electrical insulation of power cables in contact with humidity. Particularly comprehensive reviews of treeing phenomena are recently given by Eichhorn[2] and Ieda[3].

According to Meyer and Filippini[1], water-treeing is generally thought to occur in three sequential steps: (1) absorption of water to form a water-filled pocket; (2) initiation of a channel from this pocket; and (3) propagation and growth of channel. It is generally observed that high a.c. or d.c. voltages favour the formation of water-trees[2].

We propose that the osmotic pressure resulting from the absorption of water by water-soluble inclusions present in the insulation can at least be a contributing factor in the type of water treeing discussed by Meyer and Filippini[1]. The osmotic pressures which develop can be substantial and can lead to the formation of numerous cracks surrounding the inclusion, which are remarkably similar in appearance to water-treeing formed in the presence of electric fields. Although osmotic pressure alone is sufficient to produce the effect, it is believed that the presence of an electric field increases the rate and possibly the size of the water trees which ultimately form.

Formation and growth of water trees

In a previous paper[4], it was shown that inclusions of water soluble substances imbedded in a rubber (silicone) led to the formation of cracks within the rubber when moisture is present. Briefly, the process is as follows: water diffuses into the polymer and comes into contact with the inclusion. The inclusion begins to dissolve and form a near-saturated solution. During this process a cavity forms around the inclusion which acquires a spherical or near spherical shape as more water diffuses into the cavity. The driving force for this process is the difference in chemical potential of the water in the bulk phase outside and the water as solvent for the inclusion inside the polymer. Since the chemical potential of water inside is less than that outside, water moves into the cavity. This movement of water gives rise to a pressure termed the osmotic pressure and this pressure is exerted by the solution on the boundary of the cavity. The polymer behaves as a semipermeable membrane which prevents the dissolved inclusion from leaving the cavity. At equilibrium, the osmotic pressure equals the hydrostatic pressure exerted by the polymer on the surface of the cavity. These osmotic pressures are substantial and can reach values of a few thousand atmospheres.

A subsequent paper[5] showed how the equilibrium water uptake by this osmosis mechanism can be estimated and it was pointed out that the important variables to consider are the shear modulus of polymer and the solubility of the inclusion material in water.

In the initial study[4], it was observed that the cavities often ruptured to form disc-shaped cracks. Apparently this process occurred because the initial dry inclusions