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Preparation of crosslinked polystyrene beads including oligo(oxyethylene) chain as crosslinking agent and their use as phase transfer catalyst

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SUMMARY

α,ω-bis(p-vinylbenzyl)-terminated oligo(ethylene oxide)s (I) with oxyethylene repeating units of 1 - 21 were prepared. Suspension copolymerization of I with styrene gave the insoluble crosslinked polymer beads (II) which were found to act as highly effective phase transfer catalysts in the reaction of solid potassium phenoxide with 1-bromobutane in toluene.

INTRODUCTION

Poly(ethylene glycol)s (PEG) and their derivatives are known to complex some alkaline cations and act as phase transfer catalyst (PTC) in a number of reactions (1,2). We have demonstrated in the preceding paper (3) that a variety of graft copolymers of styrene and ethylene oxide having well-defined structure and composition prepared by the use of macromonomer techniques are very effective catalysts in Williamson ether synthesis and indeed are more effective than poly(ethylene oxide) itself (3). Catalytic activity of block copolymers of the same monomers was also examined by Sherrington et al (4). It is always important to develop insoluble polymeric reagents or catalysts because of their extreme ease of handling and recycling if their reactivity or activity are at least as same as those of usual small molecular soluble reagents or catalysts. In recent years there have been a number of papers describing the use of solid support bonded oligo(ethylene oxide)s as PTC (5). The work completed thus far involves the immobilization of oligo(ethylene oxide)s to divinylbenzene-styrene copolymer by reacting oligo(ethylene glycol) derivatives with a chloromethyl moiety in the polystyrene chain. By this method the resulting degree of substitution or loading of oligo(ethylene oxide)s is somewhat limited. Particularly, with the oligo(ethylene glycol)s of relatively high molecular weight, the loading achieved was considerably lower than the original level of chloromethylation as indicated by elemental microanalysis (6).

In our preliminary investigations we have prepared a new type of polystyrene resins (II) containing oxyethylene chain

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*To whom offprint requests should be sent as crosslinking agent. A simple structure of the crosslinking agent (I) is composed of both terminal styryl groups and oligo(oxyethylene) chain. This structure is easily prepared by coupling of p-vinylbenzyl chloride with the sodium salts of the corresponding oligo(ethylene glycol)s. A variety of chain lengths of the crosslinking agent can be prepared by use of commercially available oligo(ethylene glycol)s. The content of oligo(oxyethylene) chain in the polymer is also readily controlled by chose of the ratio between styrene and I in polymerization. Copolymerization of styrene with I gave crosslinked polymers II, which may be applied to PTC in many reactions. Homopolymerization of this crosslinking agent can achieve the markedly high content of oxyethylene chain in the crosslinked polymer which was quite difficult when oxyethylene chains are introduced by usual polymer supporting method. Since both terminals of oligo ethylene glycols are fixed in the crosslinked polymer oligo(oxyethylene) chains could form cage structures or analogous structure of crown ethers which are known to be efficient PTC in a number of reactions (7). In the reaction of solid potassium phenoxide with 1-bromobutane in toluene these polymers (II) exhibited very high catalytic activities. In this paper we describe the preparation of the new polystyrene beads containing oligo(oxyethylene) chain as crosslinking agent and their use as PTC in Williamson synthesis.

EXPERIMENTAL

N,N-Dimethylformamide (DMF), toluene, and 1-bromobutane were purified by distillation from CaH_2. Diethylene glycol, triethylene glycol, tetraethylene glycol, oligo(ethylene glycol)s (PEG400, PEG600, PEG1000, and PEG1500), poly(vinyl alcohol), and sodium hydride (NaH) were used without purification. p-Vinylbenzyl chloride was prepared by successive chloromethylation and dehydrohalogenation of 2-bromoethylbenzene as described by Kondo et al (8). a,a-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Potassium phenoxide was prepared by a literature procedure (9).

Crosslinking agent containing oligo(oxyethylene) chain I (n=3): A mixture of 3.88 g (20 mmol) of tetraethylene glycol and NaH (1.1 g, 46 mmol) in 40 ml of dry DMF was stirred at room temperature for 1h. After DMF solution of p-vinylbenzyl chloride (7.05 g, 46 mmol) was added to the above mixture stirring was continued at room temperature for 24h. Workup was effected by addition of water to the reaction mixture. After removal of DMF by distillation under reduced pressure at 50°C the water layer was extracted with ether (3 x 50 ml) and the extract was washed several times with water; the ethereal extracts were dried over $MgSO_4$ and concentrated to afford a product which was purified by column chlomatography using chloroform as eluent to afford a viscous liquid of the pure I(n=3) (6.9 g, 81%). ^1H-NMR($CDCl_3$): 3.63(br 16H), 4.52(s 4H), 5.21(d 2H), 5.71(d 2H), 6.67(q 2H), 7.27(d 4H), 7.36(d 4H). Anal. Calcd. for $C_{26}H_{34}O_5$: C,73.21; H,8.03. Found: C,73.18; H8.05. IR(cm^{-1}): 1630(C=C stretch), 1100(C-O-C stretch).

Crosslinked polymer IIe: To a well stirred solution of 0.3 g of poly(vinyl alcohol) (degree of polymerization 2000; degree of saponification 78 - 82 mol%) in 100 ml of water cooled to 0°C was added a solution of 1.28 g of I(n=3), 2.8 g of styrene, and 0.1 g of AIBN. After 1h stirring at 0°C to homogenize the size of beads formed, the temperature was raised to 70°C and the reacion mixture was stirred for 48h. The resulting beads were filtered and washed with water. Further washing with water-methanol, methanol, tetrahydrofuran, and methanol followed by drying under reduced pressure at 40°C afforded the desired copolymer (yield 3.8 g). The infrared spectrum of the beads included the C-O-C absorption at 1100 cm^{-1}. Anal. Calcd. for $(C_8H_8)_{0.90}(C_{26}H_{34}O_5)_{0.10}$: C,86.30; H,7.83. Found C,86.22; H,7.90.

Williamson ether syntheses: Reaction between potassium phenoxide and 1-bromobutane were carried out on a small scale as previously described (3) and were monitored employing normal quantitative G.L.C. methods. Initial rates were calculated from the gradients of 1-bromobutane decay curves. Yields of phenyl butyl ether were also determined by G.L.C.

RESULTS & DISCUSSION

Preparation of crosslinking agents (I) and their polymerization are shown in Scheme 1. Oligo (ethylene glycol)s of n=1 to 21 were chosen for their preparations. Suspension copolymerization of I with styrene afforded the insoluble resin having the spherically symmetrical bead form. Variety of oxyethylene chain content in the polymer can be obtained. By the use of these crosslinking agents, flexible structure of crosslinkages are realized, which gives swellable and mechanically stable resins even when degree of crosslinking is very high. Homopolymerization of I under the same conditions as above were also possible to make the insoluble polymer beads (IIc, IIf), which contain markedly high content of oxyethylene chain in the resin. Homopolymerization of the crosslinking agent with a long oxyethylene chain of molecular weight more than 1500 (>PEG 1500) gave a water soluble polymer which gave rise to difficulties of isolation and purification.

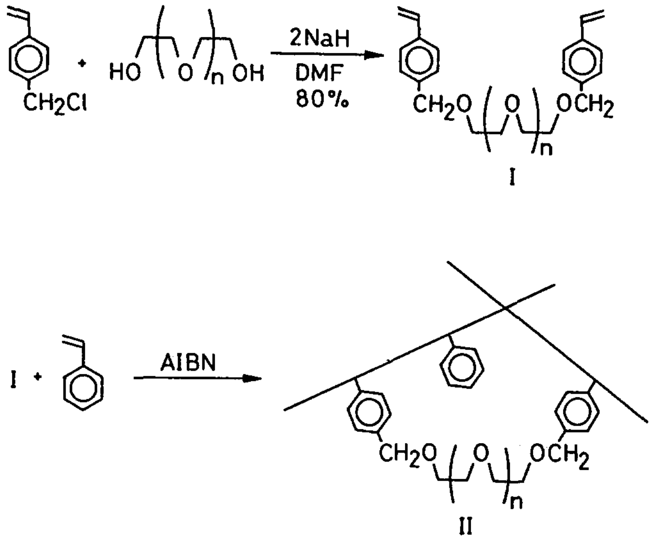
In order to estimate the phase transfer activity of these polymer beads they were used as PTC in Williamson synthesis (Scheme 2). The effectiveness of the polymeric catalysts (II) was summarized in Table. In the absence of

Table Catalytic activity of the polymers including oligo(oxyethylene) chain as crosslinking agent

Catalyst	n[c]	[St] : [I]	[OE][d] / [Ph][e]	Yield of PhOBu[a] (%)	Initial rate[b] x 10^5 (Ms^{-1})
None	-	-	-	4.2	0.09
PEG1000	-	-	-	90	2.6
18-Crown-6	-	-	-	100	11.5
IIa	1	90 : 10	0.18	10	0.7
IIb	1	50 : 50	0.67	17	0.8
IIc	1	0 : 100	1.00	22	0.9
IId	2	90 : 10	0.27	45	1.4
IIe	3	90 : 10	0.36	62	2.2
IIf	3	0 : 100	2.00	98	8.1
IIg[f]	7.7	60 : 40	2.27	100	19
IIh[g]	12.2	70 : 30	3.00	100	45
IIi[h]	21.3	90 : 10	1.92	100	10
IIi[i]	21.3	90 : 10	1.92	100	10

a After 3h. b From 1-bromobutane decay curves. c Number of (CH_2-CH_2-O) units in I. d Number of (CH_2-CH_2-O) units in the catalyst. e Number of phenyl rings in the catalyst. f Derived from PEG 400. g Derived from PEG 600. h Derived from PEG 1000. i Recovered catalyst was used.

catalyst no significant reaction occurs. Catalysts containing relatively short chain of oligo(oxyethylene)s (**IIa**, **IIb**, and **IId**) showed poor activity in this reaction, even if the catalyst has high content of oxyethylene chain (**IIc**). With **IIf**, **IIg**, **IIh** or **IIi** virtually quantitative conversions can be achieved in conveniently short reaction time. Although these catalysts are insoluble in the solvent they swell very well and work well as PTC in Williamson synthesis. Moreover, the insolubility of the catalyst facilitates the ease of its recovery. These catalysts



Scheme 1

$$\text{nBuBr/toluene} \quad + \quad \text{KOPh(solid)} \xrightarrow{\text{PTC}} \text{nBuOPh} \quad + \quad \text{KBr}$$

Scheme 2

could be recovered by filtration and with little additional work be ready for use again. Recovered polymer showed the same activity as original one (IIi). The higher content of I, namely, content of oxyethylene chain in the catalyst produces rate enhancement (**IIa**, **IIb**, and **IIc**; **IIe** and **IIf**). Significant catalytic activity was obtained from **IIh** which has the highest ratio of oxyethylene unit to benzene ring ([OE]/[Ph]). Crosslinking agent of short oxyethylene chain could not achieve such a high value of [OE]/[Ph] even on **IIc**. It appears that the enhanced catalytic activity is associated with increased content of oligo ethers. These tendencies are paralleled somewhat with the previously described copolymers of styrene with ethylene oxide.3) Indeed with these species the reaction rate is superior to that using equivalent moles of 18-crown-6 ether, and this represents one of the few examples where a polymeric catalyst is more active than an already highly active low molecular weight species.

Catalytic activities of the polymers (II) for other reactions such as ester formation, carbene reactions, C-C bond formations, oxidations and reductions are currently under investigation.

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