A novel synthesis and characterisation of poly{1-[4-(benzo-9-crown-3-4'-ylaminosulfonyl)phenyl]ethylene} as phase transfer catalyst

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New soluble polystyrene crown ether structure as phase transfer catalyst was prepared by the reaction of styrene-4-sulfonyl chloride with 4-amino, benzo-9-crown-3- and then resulting monomer *N*-(benzo-9-crown-3-4'-yl)styrene-4-sulfonamide was polymerised with benzoyl peroxide in THF solvent under nitrogen and reflux conditions. The monomer and the polymer were identified by spectroscopic methods and also molecular weight of the polymer was determined by GPC and rate of formation of the polymer-bound lithium crown ether from the soluble polymer and aqueous LiOH was investigated.

Keywords: crown ether, phase transfer catalyst, gel permeation chromatography

Polymer-supported crown ethers have been used for separation of some metal cations, anions, and organic compounds in analytical chemistry.[1-3] It is also well known that insoluble polystyrene beads carrying pendant crown ether group as well as pendant quaternary ammonium or phosphonium salts can be used as phase transfer catalyst in liquid–solid–liquid heterogeneous organic synthesis.[4,5] It has been suggested that polystyrene containing crown ethers and mono azacrown ethers were used as phase-transfer catalysts for dehydrohalogenation, addition and substitution reaction and other organic reaction.[6] The major advantages of the polymer-supported phase transfer catalyst[7-10] are: (1) ease of separation from reaction mixture by filtration; and (2) recycling of the catalyst. This paper describes the synthesis of such polymeric crown ether by direct in this new method.

We first prepared the monomer of N-(benzo-9-crown-3-4'-yl)styrene-4-sulfonamide (III) from the reaction of styrene-4-sulfonyl chloride (I) with 4'-aminobenzo-9-crown-3 (II)[11,12] in the presence of triethyl amine in THF solvent (Scheme 1).

The polymer poly {1-[4-(benzo-9-crown-3-4'-ylaminosulfonyl) phenyl] ethylene} was synthesised from polymerisation of monomer (III) by benzoyl peroxide in THF solvent (Scheme 2).

The effect of phase transfer catalytic of the polymer was investigated by lithium hydroxide (Fig. 1).

In conclusion, the preparation and characterisation of the poly{1-[4-(benzo-9-crown-3-4'-ylaminosulfonyl)phenyl] ethylene} was investigated and we concluded that this novel polymer was able to act as a phase transfer catalyst.

Experimental

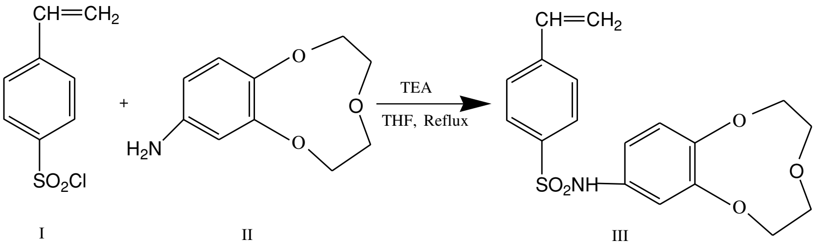
Instruments

Infra-red spectra were taken on a Shimadzu 435-u-04 spectrophotometer using KBr pellet. H NMR spectra were recorded on a JEOL FT-NMR 90 MHZ spectrophotometer using $CDCl_3$ as solvent. The molecular weight of the polymer was determined using a waters 2000 GPC analysis instrument (mobile phase: THF, Flow: 1.0 ml/min, columns: styragel 6HT, 5HT, 2HT, column temperatures: 30 °C and using a calibration plot constructed with polystyrene Standards), the mass spectrum was taken on a Varian spectrophotometer CP 3800, C.H.N and sulfur content were determined subsequently by C.H.N analyser model LECO 600 and SC132.

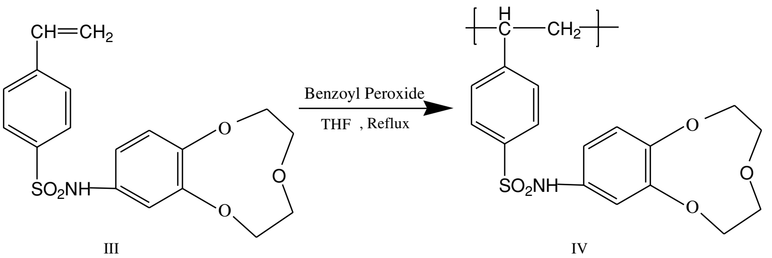
Monomer synthesis

Preparation of N-(benzo-9-crown-3-4'-yl)styrene-4-sulfonamide(III)

A mixture of 3g (0.015 mol) of compound (II), 5 ml of triethylamine and 50 ml of THF were placed in a two necked flask equipped with a reflux condenser, dropping funnel and a heater-stirrer then 3.54 g



Scheme 1



Scheme 2

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(0.018 mol) styrene-4-sulfonyl chloride (I) dissolved in 20 ml of THF was added to flask at ambient temperature gradually. The solution was refluxed for 3 h under nitrogen; the salt of triethylammonium chloride was filtered. The obtained solution was evaporated under reduced pressure and the resulting waxy product was washed with *n*-hexane. The yield of the product was 80% (4.44g).

IR (KBr) ν (cm^{-1}): N–H (3300 cm^{-1}), O=S=O (1370, 1170 cm^{-1}), C–O (1157 cm^{-1}).

^{1}H NMR ($CDCl_3$), δ(ppm): 8.18(S,1H), 7.20–7.6(q, 4H), 6.1–6.7(m, 3H), 5.1–5.7(q, 3H), 3.7–4.1(d,8H). M.S (EI): $M^{\cdot +}$(361).

$C_{18}H_{19}NO_5S$ requires: C 59.83%, H 5.26%, N 3.88%, S 8.86%. (Found): C (59.70%), H (5.21%), N (3.55%), S (8.5%).

Polymer synthesis

Synthesis of poly{1-[4-(benzo-9-crown-3-4'-ylaminosulfonyl) phenyl] ethylene} (IV)

A round bottom 50 ml flask was charged with 30 ml of THF, 2.00 g of the monomer (III) and 0.10 g of benzoyl peroxide. The mixture was refluxed under atmosphere of nitrogen for 12 h and with rotatory evaporator separated THF. The polymer was purified and precipitation by using tetrahydrofuran/water and then dried under reduced pressure at 60°C for 20h. The yield of obtained polymer was 97%.

M.p. 140°C GPC: Mn = 248317, Mw= 347508, Mz= 443158, Mz+1=568170, PDI = 1.39 ^{1}H NMR ($CDCl_3$), δ (ppm): 7.5–9 (b, 8H), 2.1–4.8 (b, 8H), 0.5–1.6 (b,3H). IR (KBr) ν (cm^{-1}): N–H (3300 cm^{-1}), O=S=O (1370,1170 cm^{-1}), C–O (1157 cm^{-1}).

Reaction of polystyrene containing crown ether unit (IV) with lithium hydroxide under two-phase condition

A 50-ml three-necked flask was charged with polystyrene containing crown ether unit (10 mmol) and 20 ml of toluene. The mixture was stirred mechanically at 50°C for 10 min and allowed to stand. A 50 ml aqueous LiOH, 1M (50 mmol) was added into the mixture immediately and heated at 50°C. The two-phase mixture was stirred (400 rpm) at 60°C for a fixed time and allowed to stand. Then, 5.0 ml of organic phase was mixed with 10.0 ml HCl 0.5M (5 mmol) in dioxane. The mixture was titrated with 0.01M methanolic NaOH using congo red as an indicator. The complex concentration in the organic phase was calculated from the HCl concentration of the original and resulting solution (Fig .1)

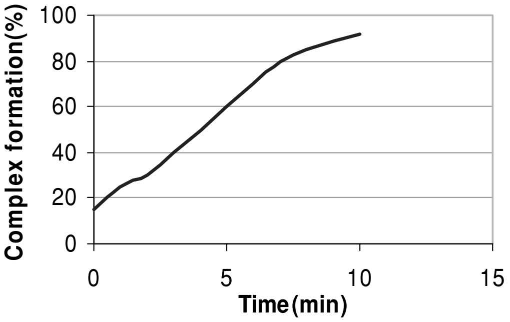

Fig. 1 Complex formation from polymer V and aqueous LiOH.

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