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Poly(*p*-styrenesulphonamide) as a New and Selective Catalyst for Bromination of Various Aromatic Compounds

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ABSTRACT

The objective of the present work was preparation of poly(*p*-styrenesulphonamide) that can be used as a catalyst for bromination of aromatic rings, such as benzene, toluene, isopropyl benzene and bromobenzene. Poly(*p*-styrenesulphonamide) can be synthesized from radical polymerization of *p*-styrenesulphonamide with the use of azobisisobutyronitrile (AIBN) as an initiator. *p*-Styrenesulphonamide was prepared from commercial 4-vinylbenzene sulphonic acid sodium salt (CH_2=CH.$C_6H_4SO_3\bar{N}\dot{a}$), phosphorus pentachloride, and ammonia. Poly(*p*-styrenesulphonamide) synthesized can be used in equimolar amounts as a polymeric catalyst, and it catalyzes a wide range of bromination reactions. Then the brominated product is separated and the polymer is recovered, which can be used in another process for bromination of other aromatic rings. One of the advantages of this polymer is that the bromination of aromatic rings takes place without brominating the alkyl substitution on aromatic ring. Also in comparison with catalysts which so far have been applied for bromination of aromatic compounds, this polymer, as catalyst, has many advantages, e.g. high recovery, reuseability, selectivity and stability when exposed to moisture and air.

Key Words: bromination, selective catalyst, polymer supports, halogenation, aromatic rings

INTRODUCTION

Hydrogen substitution by halogen is an important synthetic electrophilic aromatic substitution. Molecular halogens only attack the active aromatic compounds. Many of such reactions take place in presence of Lewis acids. The halogen-Lewis acid complex operates as an active electrophile.

Halogenation also occurs by a hypohalite carboxylic acid such as, acetyl hypochlorite (CH_3CO_2Cl) and trifluoroacetyl hypobromite (CF_3CO_2Br).

Polymer-supported catalysts are the most attractive type of polymer-supported species for applications in organic chemistry, because a relatively small amount of polymer can be used to transform a relatively large amount of low-molecular weight reactants [1 and 2].

The catalyst can be used in the bonded form to a polymer matrix. For example, the reaction of Wilkinson complex with supported polystyrene that is functionalized with a diphenylphosphino group. One of the advantages of polymer catalyst, over other catalysts, is the recoverability of the former.

It is shown that many homogeneous catalysts can be bonded to an organic support [3–6]. It is recognized that, when polymers are used as supports for catalysts, the reactivity and selectivity of the supported catalysts may seriously be changed by the so called polymer effects, the origins of which may be physical or chemical. Some examples of these effects have been published [7–10], for example the reaction of pyridine polymer complex is more reactive in bromination of aromatic rings than pyridine alone [11], or the reaction of halogen with various alkyl aromatics in the presence of *N*-chlorosuccinimide and poly(*N*-chlorosuccinimide) has been examined and it is observed that the aromatic substituted product is obtained [12].

It has been shown previously that poly(*p*-styrenesulphonamide) can be applied in selective chlorination reaction of aromatic rings [13] and selective oxidation of primary and secondary alcohols [14]. The main aim of this work is application of poly(*p*-styrenesulphonamide) as a polymer catalyst useful in selective bromination reaction of aromatic rings.

So far several brominating reagents for aromatic rings are reported [15 and 16].

The advantage of polymer-supported bromination reagent to other brominating reagents is that the regiochemistry of the bromination of various aromatic rings can be controlled, for example as in substituted phenols [17].

EXPERIMENTAL

p-Styrenesulphonamide was prepared from commercial 4-vinylbenzene sulphonic acid sodium salt, phosphorus pentachloride, and ammonia (Fluka), according to the literature [18], and melting point of *p*-styrenesulphonamide was identified and found: 134–136 °C.

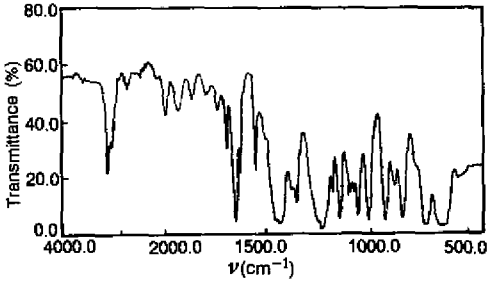


Figure 1. IR Spectrum of *p*-styrenesulphonylchloride.

In polymerization of *p*-styrenesulphonamide we used the solution method and AIBN as a radical initiator. The polymer was identified by IR, NMR, and molecular weight determination, $\bar{M}_n$, by functional group titration, which was found: 2893.5. The melting point of polymer was identified and found: 284–287 °C.

Bromination of Benzene in the Presence of a Catalytical Amount of Poly(*p*-styrenesulphonamide)

The polymer (0.25 g) was added in DMSO (5 mL) and benzene (28.4 mL) in a three necked flask with stirring and cooled in an ice bath. The environment around it was kept dark. Bromine (20 mL) was added to the solution flask with stirring. With addition of bromine an exothermic reaction began and HBr gas was liberated from the solution. After that, the solution was heated for 1 h to

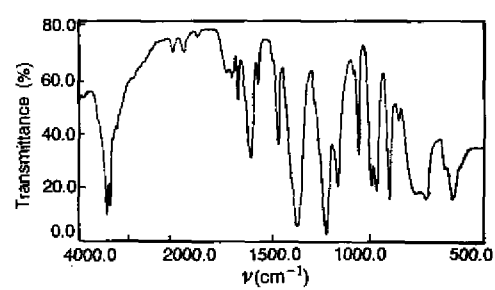


Figure 2. IR Spectrum of *p*-styrenesulphonamide.

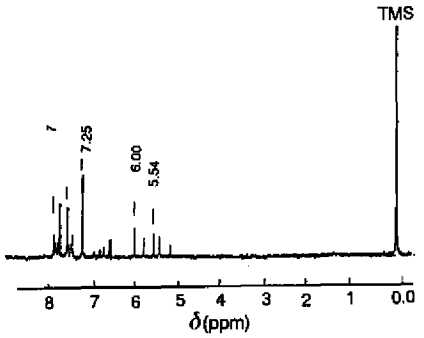


Figure 3. ^{1}H NMR Spectrum of *p*-styrenesulphonamide.

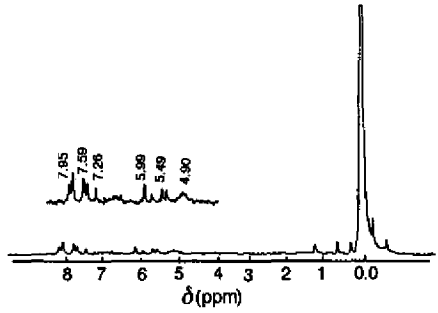


Figure 5. ^{1}H NMR Spectrum of poly(*p*-styrenesulphonamide).

25–30 °C. Then the temperature of solution was raised to 65–70 °C until all the unreacted bromine came out from solution. The bromobenzene obtained was separated by distillation, and the compound was identified by NMR and IR. The yield of reaction was 75%. The polymer was separated by vacuum distillation from DMSO and was washed with acetone and it was finally dried under vacuum at 60 °C.

Bromination of Benzene in the Presence of Recovered Poly(*p*-styrenesulphonamide)

The polymer (0.12 g) was added in DMSO (3 mL) and benzene (14.2 mL) in a three necked flask with stirring and cooled in an ice bath. Bromine (10 mL) was added to the solution and it was treated as in the above way.

The compound was identified by NMR and IR. The yield of reaction obtained was 62.6%.

Spectroscopic Analysis

IR and NMR spectra were recorded using a Shimadzu 435-U-04 spectrophotometer (KBr pellets) and a 90 MHz Jeol FT-NMR spectrometer, respectively. NMR chemical shifts were measured relative to TMS.

p-Styrenesulphonylchloride

IR spectrum showed ν(S=O) absorptions at 1360 and 1180 cm^{-1} for asymmetric and symmetric stretchings, respectively (Figure 1).

p-Styrenesulphonamide

The IR spectrum of *p*-styrenesulphonamide showed ν(N–H) stretching vibrations at 3240 and 3340 cm^{-1} (Figure 2). ^{1}H NMR ($CDCl_3$ TMS) spectrum showed a characteristic broad singlet δ

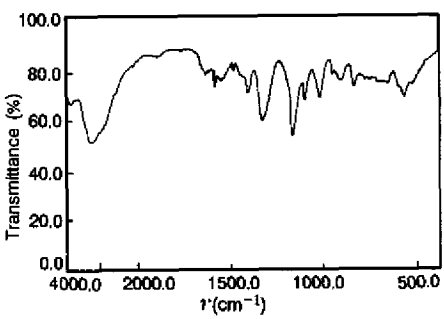


Figure 4. IR Spectrum of poly(*p*-styrenesulphonamide).

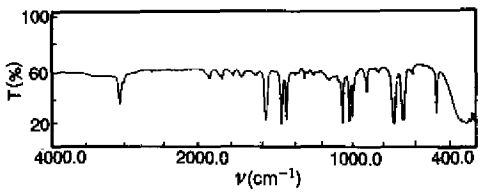


Figure 6. IR Spectrum of bromobenzene.

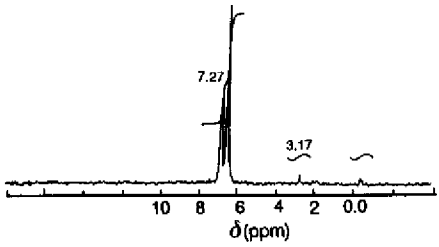


Figure 7. ^{1}H NMR Spectrum of bromobenzene.

7.25 ppm assigned to the N−H group (Figure 3).

Poly(p-Styrenesulphonamide)

IR spectrum showed ν(N−H) stretching vibrations at 3290 and 3400 cm^{-1}, and ν(S=O) absorptions at 1330 and 1170 cm^{-1} for asymmetric and symmetric stretchings, respectively, (Figure 4). ^{1}H NMR ($CDCl_3$, TMS) spectrum showed a singlet peak δ: 5.99 ppm assigned to the N−H group (Figure 5).

Bromobenzene

The IR spectrum of bromobenzene shows harmonic absorptions ν(2000−1667 cm^{-1}), a characteristic of monosubstitution of benzene ring (Figure 6).

^{1}H NMR ($CDCl_3$, TMS) spectrum of this product shows two peaks at δ: 7.01 and 7.27 ppm assigned to the substitution of bromine on the benzene ring (Figure 7).

Dibromobenzene

The IR spectrum of dibromobenzene shows harmonic absorptions ν(2000−1667 cm^{-1}), a characteristic of disubstitution of bromobenzene ring (Figure 8).

^{1}H NMR ($CDCl_3$, TMS) spectrum of this product shows peaks at δ: 6.5−7.5 ppm assigned to the *para* substitution on the bromobenzene ring (Figure 9).

RESULTS AND DISCUSSION

So far several polymer-supported catalysts are reported for halogenation of aromatic rings that

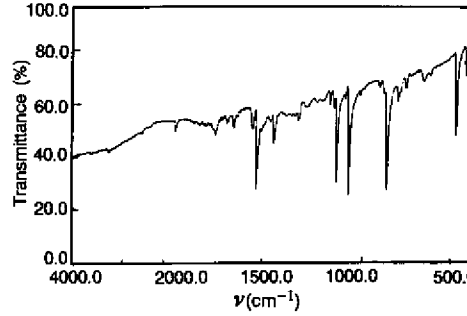


Figure 8. IR Spectrum of dibromobenzene.

usually halogenate with the use of these polymers, and consist of two steps:

– The halogenation of polymer and the separation of halogenated polymer.

– Addition of halogenated polymer to the desired compound.

This method takes a long time and is tedious. Therefore, a new method is substituted, in which we look at the polymer as a catalyst. For this purpose it is necessary to synthesize a polymer which has an electrophilic bromine. Therefore, the polymer must have an electronegative group, in order to polarize the bromine molecule. In order to have a suitable attracting group we must bond this group to another electron attracting group.

For this purpose, sulphonamide group is suitable and one of the best groups for polymerization is vinyl group.

Therefore, the best compound which could be chosen is *p*-styrenesulphonamide. After radical polymerization, a polymeric solution is obtained,

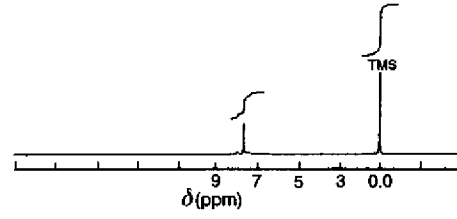


Figure 9. ^{1}H NMR Spectrum of dibromobenzene.

Table 1. Bromination of various compounds with poly(*p*-styrenesulphonamide) as a catalyst.

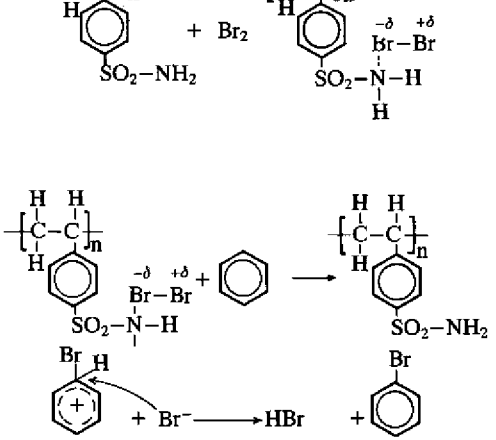
Substrate	Product	Time (min)	Yield (%)
Benzene	Bromobenzene	60	75
Bromobenzene	1,4-Dibromobenzene	86	50
Cumene	*ortho* and *para*-Bromocumene	35	88 (44 *o*, 56 *p*)
Toluene	*ortho* and *para*-Bromotoluene	45	54 (48 *o*, 52 *p*)

and bromine and the substrate are poured into the flask. The catalyst polarizes bromine and now the polarized bromine can attack the aromatic ring, and electrophilic substitution is carried out on aromatic ring (Scheme I).

According to the mechanism the polymer carries out this reaction for several times, and in this way, the catalytic role of the polymer can be shown. Then the brominated substance is separated with distillation.

The polymer is recovered by vacuum distillation and it can be used in bromination of another compound (Table 1).

These experiments have proved that the compounds with electron donating groups, show better tendency for electrophilic substitution and



Scheme I

the reactions are carried out with more intensity. Electron donating groups give electrons to benzene ring and now it shows better tendency to attract Br^+ ion and accomplish the reaction. As a result the reaction goes faster. Another problem is the orientation of substitution.

The presence of electron donating groups causes attack to occur chiefly at positions *ortho* and *para*. Benzene rings which have electron withdrawing groups show *meta* direction and less tendency for substitution. From examined compounds like nitrobenzene, benzaldehyde, benzoic acid and bromobenzene, only the latter one carries out the substitution well.

Since bromine has a dual property it deactivates benzene ring less than other compounds. Another interesting problem in bromobenzene is the amount of *para* substitution. The spectra have shown that 100% of the product is in the form of *para* substitution because bromine in bromobenzene has two effects: The first factor is a negative inductive effect that causes the less tendency of the ring for electrophilic reaction than benzene and the second factor is a resonance effect that compensates its inductive effect.

Bromine in bromobenzene from point of view of activity acts as electron withdrawing group and from point of view of orientation acts as electron donating group. On the other hand there are two positions of *ortho* substitutions, and one *para* position towards Br ion, but there are two factors cause pure *para* isomer only. The first factor is that negative inductive effect of *ortho* position is stronger and the second factor is that the huge polymer group prefers *para* position. These two factors cause the large amount of *para* product in processing bromobenzene compound.

CONCLUSION

An important advantage of this work is that the bromination of aromatic ring takes place without brominating the alkyl substitution group on aromatic ring. This advantage is attributed to the polymer effects, that can seriously change reactivity and selectivity of the bromination reaction of aromatic rings. Other advantages are the recoveribility and reuseability of the polymer.

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REFERENCES

1. Lenzoff C.C., *Chem. Soc. Rev.*, **3**, 65, 1974.
2. Arshady R. and Ledwit A., *React. Polym.*, **1**, 159, 1983, Shettington D.C., *Macromol. Syn.*, **8**, 69, 1982.
3. Pittman C.U. and Evans G.O., *Chem. Tech.*, 560, 1973.
4. Bonds W.J., Jr., Chan. Dtasekaran C., Gibbohns/Grabbs R.H., and Kroll L.C., *J. Am. Chem. Soc.*, **97**, 2128, 1975.
5. Grubbs R.H., Kroll L.C., and Sweet E.M., *J. Macromol Sci Chem*, Part A, **7**, 1047, 1973.
6. Grudds R.H., Sweet E.M., and Phisanbut S., *Catalysis in Organic Synthesis*, Academic Press, 153, 1976.
7. Challa G., *J. Mol. Catal.*, **21**, 1, 1983.
8. Baker G.L., Fritschel S.J., and Stille J.K., *Am. Chem. Soc. Org. Coat Appl. Polym. Sci. Proc.*, **46**, 687, 1982.
9. Guyot A. and Bartholin M., *Progr. Polym. Sci.*, **8**, 277, 1982.
10. Capillon J., Richard A., Audebert R., and Quivoron C., *Polym. Bull.*, **13**, 185, 1985.
11. Zupan M. and Segatin N., (Department Chemistry, University Liublijana, Slovwnia). *Synth. Commun.*, **18**, 2617–26, 24, 1994.
12. Pittman C.U. and Hanes R.M., *J. Am. Chem. Soc.*, **98**, 5402, 1976.
13. Khazaei A., Mehdipour E., and Roodpeyma B., *Iran. J. Chem. & Chem. Eng.*, **14**, 2, 1995.
14. Khazaei A., Sadri M., and Mehdipour E., *Iran. Polym. J.*, **5**, 2, 1996.
15. Muathen H., (Dep. Chem., Univ. Al-Qura, Makkah, Saudi Arabia), *J. Org. Chem.*, **9**, 57, 2740-1, 1992.
16. Skrastins I., Kastron U., Cekavicus B., Sausins A., Zelotoyabko R., and Dubur G., (Inst. Org. Synt., 226006 Riga, USSR). Khim. Geterotsikl. Soedin. **9**, 1230–5 (Russ), 1991.
17. Pittman C.U., (Industry Chemical Research Center, Mississippi State University, MS, USA), *Polym. News*, **4**, 20, 114–15, 1995.
18. Yoda N., *J. Polym. Sci.*: Part A., **3**, 2229, 1965.