Synthesis and Polymerization of 4-Vinylbenzylphenylsulfone

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Abstract: The preparation of new sulfone monomer and polymer based on 4-Vinylbenzylphenylsulfone (4-VBPS) and free radical polymerization was investigated, based on the reaction of chloromethyl styrene with sodium phenyl sulfone ($phSO_2Na$) in dimethylformamide (DMF), using the phase transfer catalysts 18-crown-6. Copolymerization of the prepared sulphone monomer with p-methylstyrene was carried out at 65 ˚C. Nonpolymerizable 4-Ethylbenzylphenylsulfone was also prepared. The prepared monomers and polymers were characterized by different spectroscopic techniques, the number-average molecular weights (M_n) of the resulting polymer was found to be in the range of 70,100 -73,100, with polydispersity indices (M_w/M_n) vary from 1.8 to 1.9. Photolysis of the prepared polysulfone polymer and possible grafting of methyl methacrylate (MMA) monomer will be reported.

Keywords: 4-Vinylbenzylphenylsulfone, chloromethylstyrene, Polysulfone synthesis, free radical polymerization, copolymerization reactions.

1. INTRODUCTION

Chemical modifications are of great interest in polymer applications involving the preparation of selectively functional group monomers and polymers, as matrices for many industrial applications such as separation, catalysis, and organic synthesis [1-4].

Polysulfones, introduced by Union Carbide in 1965 was among the first thermoplastics known long term service engineering materials. These polymers have excellent resistance to creep and stress cracking, good thermoplastic properties, high softening point, low solubility in common solvents and negligible water absorption, and high glass transition temperature, polysulfone polymers are very promising functional polymers [5-7]. Polystyrene sulfonation with p-toluene sulfonyl chloride in the presence of anhydrous aluminum chloride in methylene chloride was reported [8]. Extrusion of sulfur dioxide from alkyl and aryl sulfones has proven to be a useful synthetic method for the construction of a wide variety of organic structures, the primary reaction step involves reversible cleavage to form radical intermediates which further decompose with lose of SO_2 to yield the coupling products [9].

The substitution reactions of chloromethystyrene monomer with nucleophilic reagent (**I**) N,N-dimethylformamides by using phase-transfer catalysts (PTCs) such as 18-crown-6 have been investigated [10], this method is important for the syntheses of functional polymers such as polymeric reagents, polymeric supports, and polymeric carriers.

In this article, we wish to describe the synthesis and polymerization of 4-Vinylbenzylphenylsulfone (1), copolymerization of monomer (1) with p-methyl styrene, and the photodecomposition of polymer (1) is reported.

2. EXPERIMENTAL

2.1. Materials

Sodium phenylsulfone, dimethylformamide (DMF), chloromethylstyrene, 4-methylstyrene monomer, methyl methacrylate (MMA) (Aldrich), and all solvents (Aldrich) were dried over calcium hydride and distilled before use.

2.2. Instrumentation

Ultraviolet spectra were obtained on a Unicam SP1800 Ultraviolet spectrophotometer. Infrared spectra were recorded using potassium bromide (KBr disc) with a Perkin-Elmer grating infrared spectrophotometer (Model 577). NMR spectra were taken in $CDCl_3$, on a Perkin-Elmer 60 MHZ spectrometer (Model R12B) using deuterated solvents with tetramethylsilane as the internal standard. Mass specta were measured by a V.G. Micromass 12. Elemental analyses were performed by Elemental Micro-analysis Limited Laboratories and are within the satisfactory range.

2.3. Polymerization Reactions

Selected amounts of the prepared monomer and initiator (AIBN) in dichloromethane were placed in a 12 mm diameter pyrex tube, the solution in the tubes were degassed under vacuum using freeze/thaw techniques and sealed off after three cycles. The sealed tubes

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were placed in a water bath and left for the required period immeresed in water bath at 65 °C. after the appropriate time the tube was removed, broken, and the contents poured into a large volume of methanol to precipitate the polymer. The polymer was filtered dried and weighed. The polymer yield and the rate of polymerization were determined gravimetrically based on the isolated polymer weight [11]. The number averged molecular weight (Mn) of the obtained polymer was measured on a Hewlett Packard, Model 501 High Speed Membrane Osmometer in toluene. Molecular weight distribution were determined using a Waters Associates model 200 GPC at 25 ˚C. The systems were examined in THF with a solvent flow rate of 1.0 ml /min and a polymer concentration of 1.0 mg/ml. Molecular weights were calculated with reference to polystyrene standards [12].

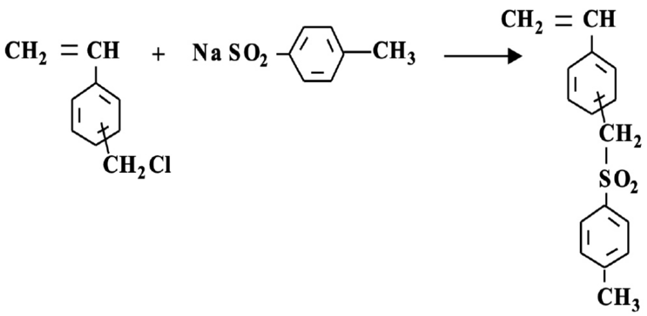
3. RESULTS AND DISCUSSIONS

3.1. Synthesis of Phenyl-4-Vinylbenzylsulfone Monomer

In a 50mm mL round bottom flask fitted with magnetic stir 10.0 gm from chloromethyl styrene was added to 200 ml dimethylformamide (DMF) containing 14.0 gm of sodium phenyl sulfone and 1.5 gm 18-crown-6. The reaction mixture was heated for 3.0 hours at 60 ˚C, then left to cool to room temperature, after that it was powered in two liters water, stir for 10 minutes, then filtered, the recovered solid was dissolved in small volume of dichloromethane and precipitated in petroleum ether (40-60 ˚C), filtered, dried to give 16.0 gm product, further purification by dissolving in small volume of dichloromethane then pouring in petroleum ether gives white solid having melting point 115 - 117 ˚C. the yield percentage was 85. Elemental analysis of for $C_{15}H_{14}\ O_2\ S_1$, of the final whit product.

Expeted: C = 69.76 H = 5.42 S = 12.40

Found: C = 69.53 H = 5.45, S = 12.50



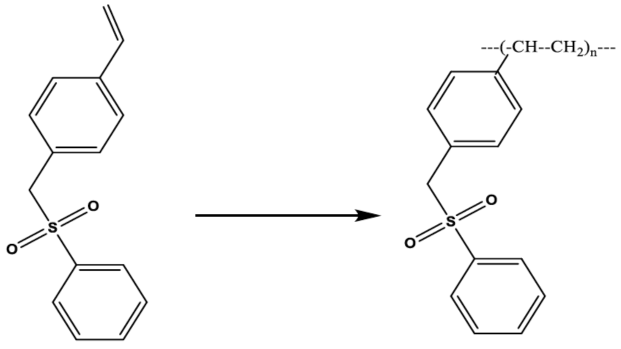
3.2. Free Radical Polymerization of Monomer 1

To each reaction tube added 0.05-gram AIBN initiator, 2.0 g Monomer (1) dissolved in 13.0 ml dichloromethane, degassed under vacuum by freeze dry technique and sealed under vacuum then placed in water bath at 65 °C for the required time, powered in 4-fold excess methanol then precipitated and filtered and dried under vacuum at room temperature.

Elemenetal analysis for the molecular formula $C_{15}H_{17}S_1O_2$ found the following:

C= 78.61%, 78.43%, H= 6.72%, 6.74%, S =7.54%, 7.58%

Polymer obtained from monomer (1) was white crystalline solid powder and found to be soluble in dichloromethane, benzene.



Monomer 1 **Polymer 1**

Figure **1** shows the results of polymerization of monomer (**1**) using AIBN at 65 ˚C, the initiator concentration 7.3x10^{-3} M, monomer concentration was 0.97M in dichloromethane. It is clear from this figure that the rate of polymerization increase with polymerization time.

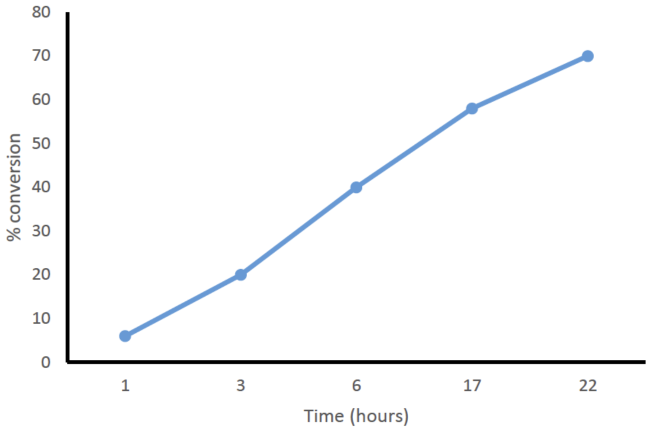


Figure 1: Polymerization of monomer (1), using [AIBN] = 7.3x10^{-3}M, at 65 °C, [M] = 0.97M in dichloromethane.

3.3. Effect of Monomer Concentration on the Polymerization

The effect of the monomer (1) concentration on the rate of polymerization based on the amount of polymer recovered) was examined through the variation of the concentration of monomer (1). In Figure **2** the conversions to polymer was increased as the concentration of the monomer increased. [AIBN] = 9.13x10-3, Time =16 hours

Figure **2** shows the correlation between the rate of polymerization Rp and the monomer concentration. It is clear from this figure that Rp is directly proportional to the variation in monomer concentrations [12].

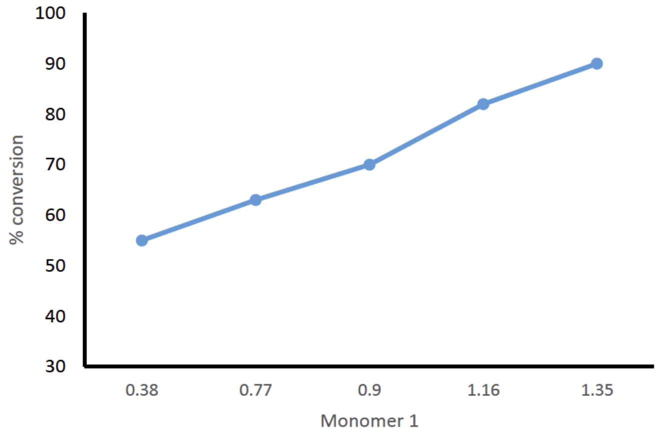


Figure 2: Effect of monomer 1 concentration on polymerization rate, Time = 16 hours, [AIBN] = 9.13×10^{-3}.

3.4. Polymerization of Monomer 1 at Various AIBN Concentration

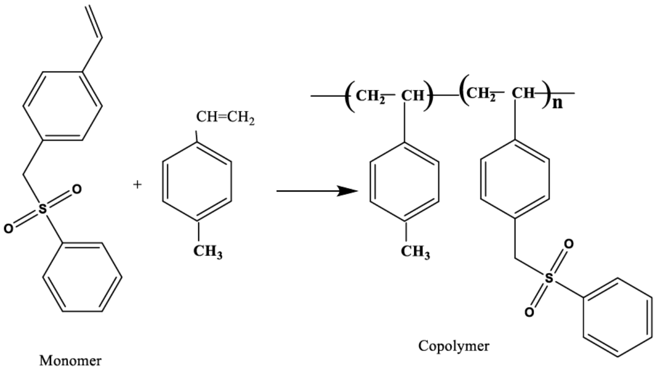
The effect of the initiator (AIBN) concentration on the rate of polymerization (R_P) was examined at 65 °C at fixed time. It was found the rate of polymerization increased as the intiator (AIBN) concentration increased. Figure **3** shows the square - root dependence of the photopolymerization rate (R_p) of monomer 1. Accordingly, the equation for R_p in the polymerization of monomer (1) by the free radical polymerization initiator (AIBN) was formulated as;

$$R_p = K[M][I]^{1/2}$$

This rate equation indicated that initiation is proceeding by a free radical mechanism [12].

3.5. Copolymerization of Monomer (1) and p-Methyl Styrene

The copolymerization of sulfone monomer (1) and p-methyl styrene (PMS) monomer was attempted by selecting certain amount of each monomer in a 12 mm pyrex tube. The concentration of the initiator (AIBN) was 4.8 $x10^{-3}$, polymerization was carried out at 65 °C, the polymerization time was 4.30 hours, the percentage conversion to polymer was calculated based on the total monomers weight was 0.78 gram as shown in Table **1** below.



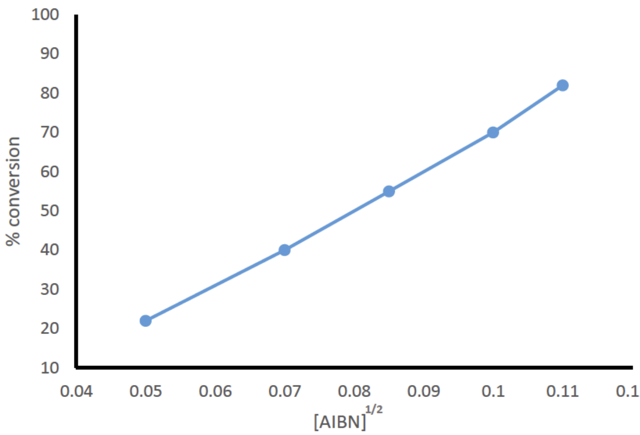


Figure 3: Effects of initiator concentration on the polymerization of monomer (1), Time is 16 hours, temperature is 65 °C.

Calculated percentage of monomer 1 in the copolymer was calculated using NMR as shown in Figure **4**.

The obtained copolymer was characterized by IR and NMR spectroscopic techniques according to the peaks; NMR delta = 4.13 ($-CH_2$ SO_2). IR (KBr): 1140,1290 cm^{-1} (SO_2 groups) as in Figure **5**.

3.6. Synthesis Ethyl Phenyl- 4-benzylsulfone (Structure 5)

$$CH_3\text{-}phSO_2Na + CH_3CH_2PhCH_2Cl \xrightarrow{-NaCl} phSO_2CH_2PhCH_2CH_3$$

The nonpolymerizable model of the sulfone monomer (1) structure (5) was prepared based on Sato *et al*. [13].

Table 1: Data on the Copolymerization of Monomer 1 with p-Methyl Styrene. Variations in the Feed Composition and the Obtained Copolymer

Exp. #	g PMS	g M1	% Monomer 1 in feed	% Conversion	% M1 in the copolymer
1	0.18	0.6	77.0	1.4	82.7
2	0.09	0.6	86.95	15.6	90.25
3	0.045	0.6	93.0	14.7	97.26
4	0.6	0.2	32.2	8.3	33.17
5	0.6	0.1	16.4	4.2	24.15
6	0.6	0.05	7.7	4.5	18.1

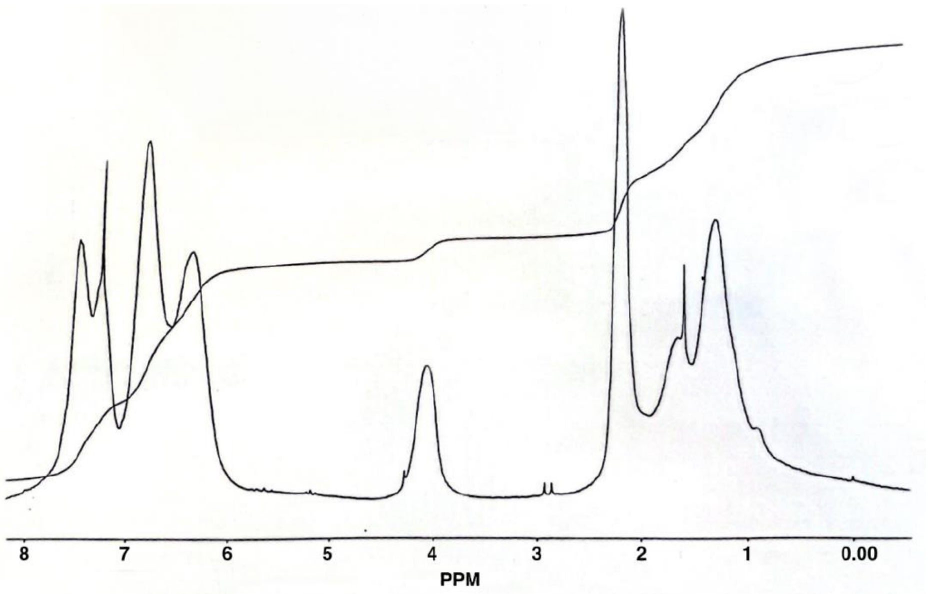


Figure 4: NMR of copolymer (p-mythyle styrene + Monomer 1 in CCl4 solvent).

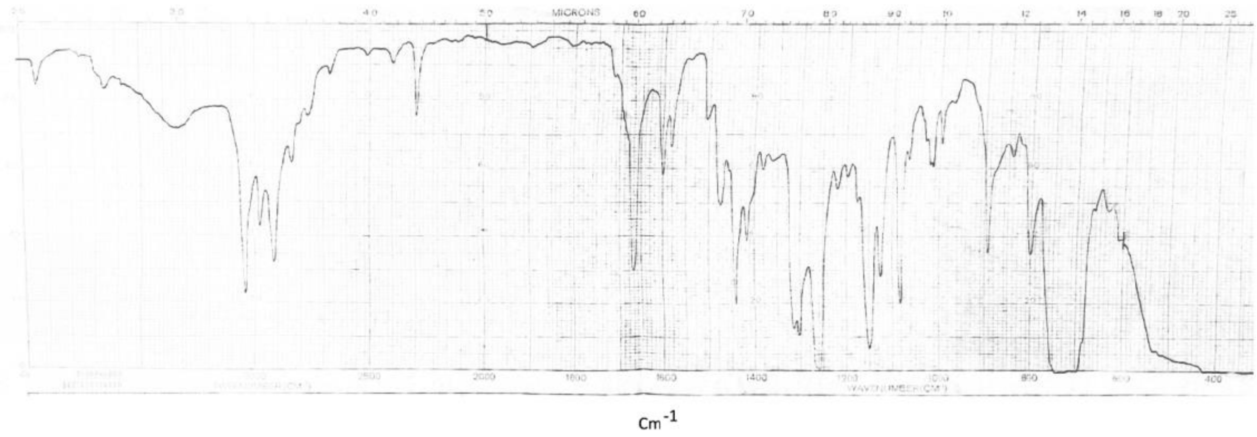
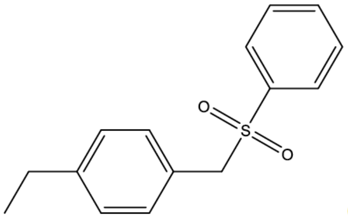


Figure 5: FTIR of monomer 1.

A solution containing 50.0 mL DMF, 2.5 gram sodium phenyl sulfone (phSO_2Na), 0.60 gram of 18-crown-6 ether, was stirred magnetically for 10 minutes, then 2.0 ml of $CH_3CH_2PhCH_2Cl$ was added slowly, the reaction mixture was left stirring at 60 ˚C for 4 hours, then cooled to room temperature, and powered in cooled water, filtered, and dried then dissolved in small volume of dichloromethane and precipitated in excess petroleum ether (40-60), after filtration and drying 3.5 gram white solid was recovered, melting point 84 - 86 ˚C. Yield % 85.



(Structure 5)

3.7. Photoextrusion of SO_2 from Polymer 3

The photoactivity of aryl sulfones was first reported by Cava *et al*. [15] Who found that upon irradiation these compounds efficiently lose molecular sulfur dioxide and yield products typical of radical coupling reactions. Extrusion of sulfur dioxide from alkyl and aryl sulfones has proven to be a useful synthetic methode for the construction of a wide variety of organic structures with ordinary light sources. Bamford *et al.* [16] examined the esterification of dextran: routes to bioactive polymers and graft copolymers.

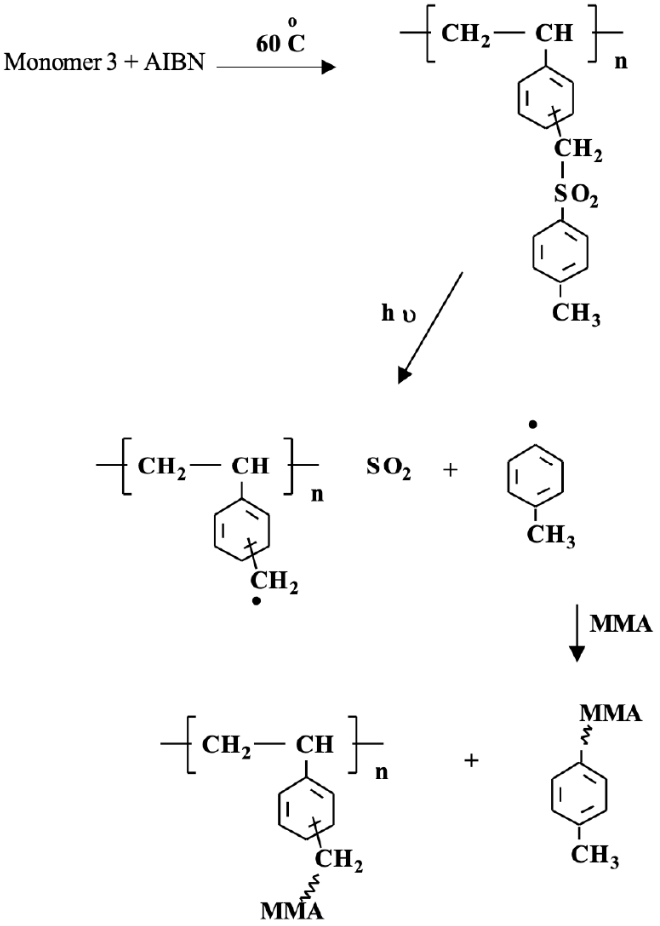
Our early interest in photochemical reactions for polymerization reactions [12] has Led us to this study for possible root to graft polymerization (Photoinitiated polymerization of vinyl monomers by benzophenone t-butyl peresters.

Photolysis of polysulfone polymer 2 in dichloromethane/benzene 40/60 V/V in Pyrex reaction tube, after degassing the reaction tube was sealed under vacuum, then irradiated from 300 nm light using merry-go- round for one hour, precipetation and isolation of the product gives the following elemental analysis for molecular formula $C_{15}H_{17}S_1O_2$

Found: C: 68.74, 68.54, H:5.48, 5.38, S:12.91

Under the same experimental conditions the photolysis above was repeated in Quartz tube the following analysis was found for molecular formula $C_{15}H_{17}S_1O_2$ found C: 89, H :5.42, S : 12.19.

Results in quartz tubes indicates the sample photolysed has lost sulfur possibly due to splitting the SO2 group (unit), (from 12.91 in Pyrex to 12.19 in quartz, which indicates that sample irradiated in quartz has lost around 15% of sulfur. Scheme 2 is proposed for the photolysis process [14].



Photolysis of sulfone polymer (1) at room

4. CONCULOSIONS

Sulfone Monomer was prepared from the reaction between chloromethylstyrene and ($phSO_2Na$), in DMF- in the presence of the phase transfer catalysts 18-crown-6 and polymerized.

Free radical polymerization and copolymerization of the sulfone monomer was carried out at 65 ^{O}C using (AIBN). Photolysis of the sulfone polymer obtained was studies and the generated radical intermediate could be capable of initiating free radical crafting polymerization of methyl methacrylate (MMA) on the sulfone polymer prepared.

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