

PTC For Nitro Displacement of Bis (M- Nitrophenyl Sulphone) In the Synthesis a of Some New Polyethersulphone

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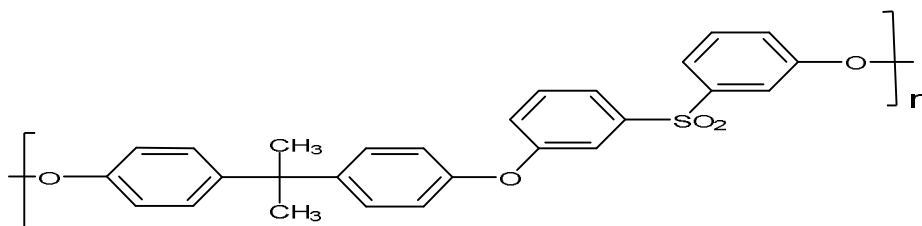
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Summary

The Synthesized polyether sulphones were carried out by interfacial polycondensation of bisphenol-A and bis (m-nitrophenyl) sulphone ,in heterogeneous system via nucleophilic aromatic substitution reaction for nito group by using various phase transfer catalyst (PTC),(benzyltributyl ammonium chloride (BTBAC),hexadecyl-tributylphos-phonium bromide (HTBPB) and dibenzo-18-crown-6) in various organic solvents (dichlorometahane , nitrobenzene and dimethyl sulphoxide). Ultrasonic irradiation was used to improve the yield and to reduce the reaction time in the present of PTC (HTBPB).



The above polymers were characterized by C, H analysis, reduce viscosity and spectroscopic methods.

Introduction

Interfacial polycondensation with various phase transfer catalysts (PTCs) such as crown ethers and quaternary ammonium and phosphonium salts for the synthesis of a variety of polymers have been studied¹⁻⁶. We have reported on aromatic nucleophilic substitution polymerization with PTCs, which led to the formation of aromatic polyethers^{7,8,9}. It has been reported that ultrasonic irradiation improved the yield and reduced the reaction times in the PTS reaction^{10,11,12}.

Here, we synthesized new polymers by PTC polymerization between bisphenol-A and bis (m-nitrophenyl) sulphone. This polymerization is promising for the growth of new markets for aromatic plastics.

Experimental

Materials

All the reagents and monomers were obtained from commercial sources (Fluka- Aldrich) or were prepared by procedures in the literature and were subjected to standard purification procedures before use.

Polymerization Method:

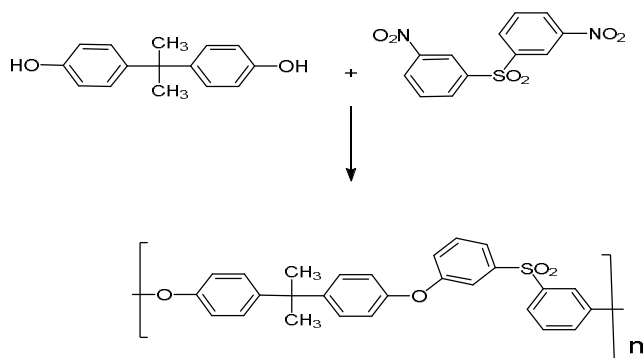
The polymers were synthesized by the reaction of Bisphenol-A and Bis (m-nitrophenyl) sulphones by using DB-18-C-6, BTBA and HTBPB as phase transfer catalyst (PTC).

To (0.56g, 2.5mmol) of purified bisphenol-A in a two necked flask equipped with thermometer and condenser, 5ml of sodium hydroxide solution NaOH(1.0N) was added with stirring, (0.05mmol) of PTC and then (0.77g, 2.5mmol) of bis (m-nitrophenyl) sulphone in (7.5ml) of organic solvent was added gradually. The polymerization was carried out by using different organic solvent at different temperatures and times. The viscous material was poured slowly into 50ml methanol and the polymer was filtrated off. High speed mixture was used in order to get polymer in a fine powdered form.

The polymer was subject to an extraction process to remove any inorganic salts that are trapped in the polymer. This was achieved by using a soxhlet extractor and boiling water. The salt is assumed to be soluble in hot water since the boiling water penetrates and swells the polymers. This extraction process was allowed to proceed for 6 hours followed by drying in a vacuum oven at 70°C for 24 hours as shown in tables (1, 2, and 3).

The same polymerization was repeated by using ultrasonic (U.s) bath with some samples.

Table [I]:-Synthesis of polymer I via nitro displacement BTBAC by using BTBAC



Sample No.	Organic solvent	Temp. °C	Tim. hr.	U.s Tim. hr.	Yield %	Polymer melt Temp. C	[η] dL.g ⁻¹
1L	CH ₂ Cl ₂	27	24	10	69	205 -201	0.3
2L	CH ₂ Cl ₂	50	4	-----	46.4	200	0.2
3L	CH ₂ Cl ₂	27	48	-----	54	201-205	0.52
4L	PhNO ₂	27	48	-----	69	205-208	0.72
5L	PhNO ₂	60	10	-----	63.6	200 -202	0.22
6L	(CH ₃) ₂ SO	27	48	-----	38	200 - 204	----
7L	(CH ₃) ₂ SO	70	10	-----	38	200 - 204	0.32
8L	PhNO ₂	40	-----	10	20	200 - 208	1.06
9L	(CH ₃) ₂ SO	40	-----	10	20	203 - 210	0.54

The Polymerization was carried out with (2.5 mmol) of bisphenol-A in 5ml of aqueous alkaline solution (NaOH 1.0 N) and (2.5 mmol) of bis (m-nitrophenyl)Sulphon in 7.5ml of organic solvent in the presence of (0.05 mmol) BTBAC used as PTC.

(a) [η] = Reduced Viscosity.

(b) Measured at concentration 0.5g.dL⁻¹ in DMSO at 30°C.

(C) Stirring at room temperature for 24 hours and U.s For 10 hours.

(d)U.s Ultra sonic

Table [2]:- Synthesis of polymer I via nitro displacement by using HTBPB

Sampl. No.	Organic solvent	Temp. C	Time hr.	U.s Time hr.	Yield %	Polymer melt Temp. c	[η] b dL.g ⁻¹
10L	PhNO ₂	70	10	-----	62	198 -202	0.78
11L	(CH ₃) ₂ SO	70	10	-----	20	202 -204	0.54
12L	PhNO ₂	23	48	-----	40.3	196 - 208	1.52
13L	(CH ₃) ₂ SO	23	48	-----	30.2	198 -210	0.66
14L	PhNO ₂	40	-----	10	36.2	198 -210	0.64
15L	(CH ₃) ₂ SO	40	-----	10	10.2	198 -205	0.37

The polymerization was carried out with (2.5 mmol) of bisphenol-A in 5ml of aqueous alkaline solution (NaOH 1.0 N) and (2.5mmol) of bis (m-nitrophenyl) sulphone in 7.5 ml of organic solvent in the presence of (0.05mmol) HTBPB used as PIC.

(*) Measured at concentration 0.5g.dL^{-1} in DMSO at 30°C .

Table [3]:- synthesis of polymer I via nitro displacement by using DB-18-C-6

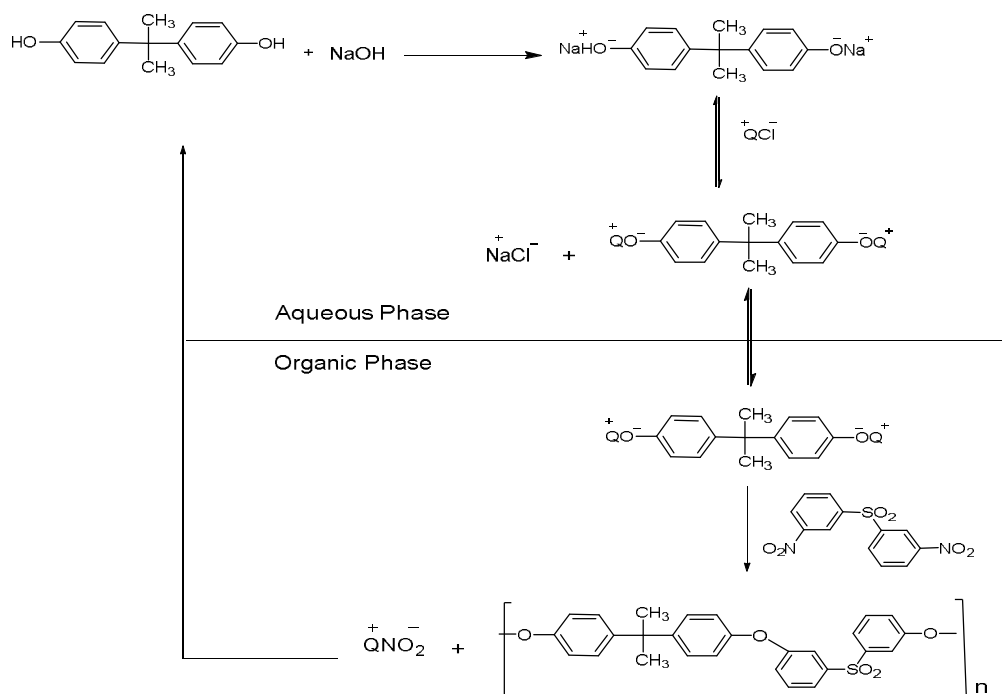
Sample Number	Organic solvent	Temp. C°	Time hr.	Us. time hr.	Yield %	Polymer melt Temp.DC	$[\eta]^*[\text{dL.g}^{-1}]$
16L	PhNO ₂	10	48	---	55.4	202-210	0.32
L17	PhNO ₂	70	10	---	57.2	202-212	0.46
L18	PhNO ₂	40	----	10	59	198-214	0.12
19L	(CH ₃) ₂ SO	10	48	---	53.5	200-215	2.58
20L	(CH ₃) ₂ SO	70	10	---	39	195 -210	0.46
21L	(CH ₃) ₂ SO	40	----	10	40	198 -210	1.13
22L	(CH ₃) ₂ SO	20	86	----	65.5	199 -207	1.18
23L	(CH ₃) ₂ SO	70	24	----	53	195 -202	0.59

The polymerization was carried out with (2.5 mmol (of bisphenol-A in 5ml of aqueous alkaline solution) NaOH 1.0N) and (2.5 mmol (of bis)m-nitrophenyl (sulphone in 7.5 ml of organic solvent in the presence of (0.05 mmo l (DB-18-C-6) used as PTC. Measured at concentration 0.5g.dL^{-1} in DMSO at 30°C .

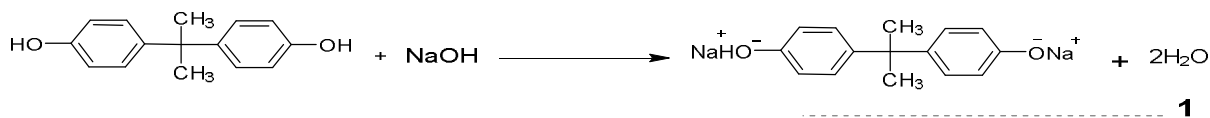
Results and Discussion

Different new polyether sulphones' have been synthesized by polycondensation polymerization of bis (m-nitro phenyl) sulphone with(bisphenol- A) in the present of various PTC in aqueous alkaline solution system at different temperatures with and without using ultrasonic ^{13 bath.}

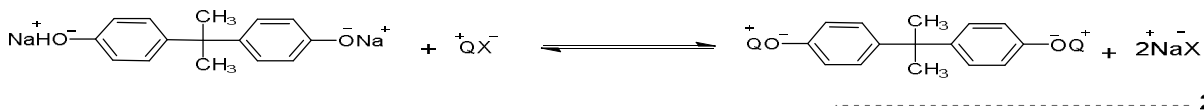
The most important rule of the solvent in the nucleophilic and electrophilic substitution reaction is the solvation of the ion-per intermediate^{(13,14,1)5}.The mechanism of the reactions by using PTC is suggested according to the following scheme for nitro replacement:



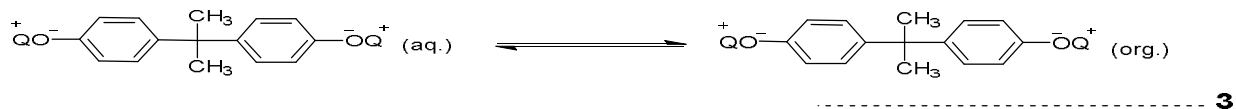
Reaction sequences (represents in equations 1-4) for the polymerization of bisphenol-A and bis (m-nitrophenyl) sulphone in a biphasic system by using PTC (BTBAC), in the presence of sodium hydroxide are (sodium hydroxide formed ion pair with bisphenol-A equ. 1) shown below:



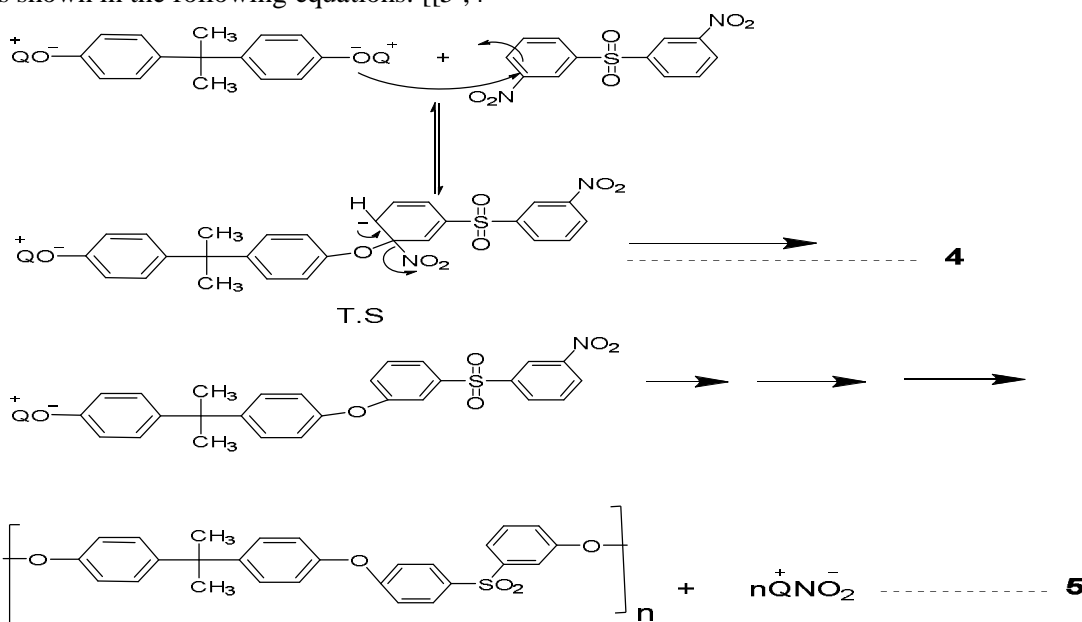
And subsequently the following reactions take place:



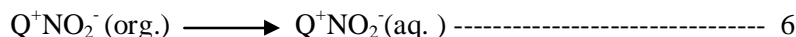
Because of the high solubility in organic phase they transfer preferentially from aqueous phase into organic phase, as shown in equation [3]



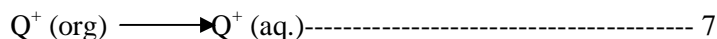
Then the phenoxide ion replaced the nitro groups by nucleophilic aromatic substitution reaction to form the polymer, as shown in the following equations. [5, 4]



The quaternary salt co-product Q^+NO_2^- will be recycled back to the aqueous phase, as shown in equation [6].



This cyclization – is repeated until all bisphenol –A are reacted with bis (Nitro phenyl) sulphone. The quaternary cation (Q+) will occur the equilibrium between the aqueous and organic, as shown in eq.[7].



The optimum conditions for the synthesis of the polymers are listed below:

The optimum conditions for the synthesis of the polymers

Sample	Alkaline solution	PTC.	Organic Solvent	Temp C°	Time hr.	U.s hr.	Yield %	Poly. melt Temp. C°	[η] dL.g ⁻¹
Poly.I(19L)	NaOH	DB-18-C-6	(CH ₃) ₂ SO	10	48	-	53.5	200 -215	2.58

The prepared polymers and monomers compositions were determined by elemental analysis techniques. The analyses were done for carbon and hydrogen. The results obtained for the prepared polymers in the heterogeneous system are shown in table [4]. A reasonable agreement between the actual and calculated data were found.

The IR. Spectra of bis (m-nitrophenyl) sulphone is tabulated in table [5]. 1 H-NMR.spectra of bisphenol-A, bis (m-nitrophenyl) sulphone, and polymer I are shown in table [6].

As shown in table [7] for polymer I, the band at (1270-1235) cm^{-1} is characteristic to the ether group (C-O-C) and no absorption in the region of hydroxyl group which appears mainly in the aromatic hydroxide absorption (3650-3200) cm^{-1} . (very broad band). The band in the region (1100 - 1010) cm^{-1} is related to the aromatic ring vibration. The significant absorption bands which are related to the polymers I are shown in table [7], The bands in the region (905-875) is related to the one free hydrogen atom and (810-775) cm^{-1} is related to three adjacent free hydrogen atoms (out of plane bending), which are characteristic to the meta substitution. The band in the position (810-865) cm^{-1} related to two adjacent free hydrogen atoms which characterize of Para substitution (16, 17, 18, 19, and 20)

Table [4]: Quantitative C, H analysis of the synthesized monomer and polymer (1)

Sample	C,H Analysis			
	Calculated		Found	
	C	H	C	H
Bis (m-nitrophenyl) sulphone	46.8	2.59	45.97	2.59
polymer I	73.3	4.98	72.78	4.05

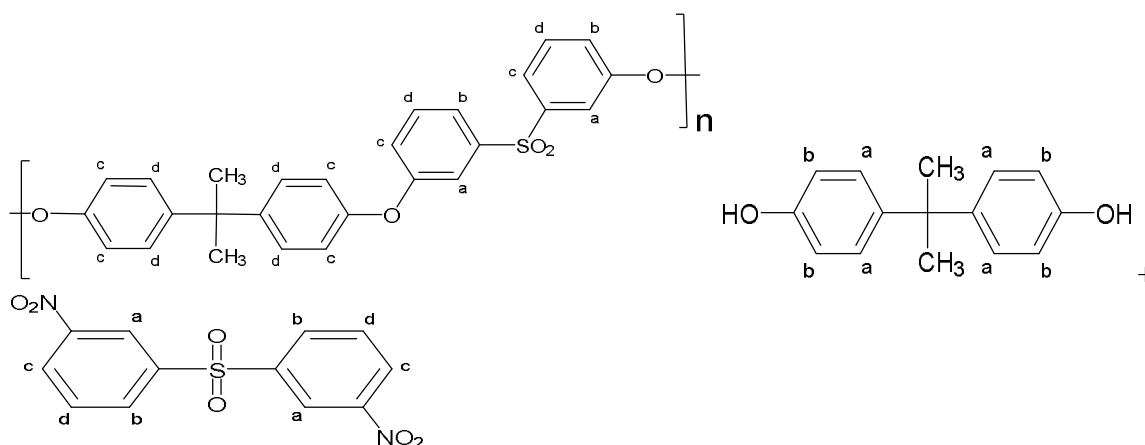
Table [5]: The location of the important absorption bands of bis (m-nitrophenyl) sulphone

Wave No. cm^{-1}	Assignment	Intensity
3090	C-H aromatic (ar.)	m. , b.
1600 & 1420	C=C ar.	v.s. , b.
1520	NO ₂ asymmetric (asy.) str.	v.s. , b.
1350	NO ₂ asymmetric (sy.) str.	v.s. , b.
1320	SO ₂ asy. str.	S. , b.
1160	SO ₂ sy. str.	S. , b.
1100	ar. ring v.	w. , b.
873	C-H for one free hydrogen atom.	m. , sh.
812	C-H for three adjacent free hydrogen atoms.	v.s. , sh.

v.s. = very strong , s. = strong , m. = medium

w. = weak , sh. = sharp , b. = broad

Table [6]: chemical shifts of ¹H-n.m.r.spectra of bis(m-nitrophenyl) Sulphone, bisphenol-A and polymer I.



Sample	Aromatic protons (δ)				Aliphatic protons	
	Proton a	Proton b	Proton c	Proton d	CH ₃ (δ)	OH(δ)
Bis(m-nitrophenyl) Sulphone	8.55(2H, s, ArH)	8.38(2H, d, J=3Hz, ArH)	8.32(2H, d, j=3Hz, ArH)	7.77(2H, t, J=9Hz, ArH)		
Bisphenol-A	6.9(4H, d, j=12Hz, ArH)	6.67(4H, d, J=12Hz, ArH)			1.55(6H, s, 2CH ₃)	
Polymer I	8.73(2H, s, ArH)	8.58(2H, d, J=3Hz, ArH)	8.51(6H, d, J=3Hz, ArH)	7.96(6H, t, J=9Hz, ArH)	7.96(6H, t, J=9Hz, ArH)	

Table [7]: The location of important absorption bands of the polymer I.

Wave No.cm ⁻¹	Assignment	Intensity
3050	C-H ar. .	m. , b.
2940	C-H CH ₃ .	s. , sh.
2860	C-H CH ₃ .	S , sh.
1585 & 1510	C=C ar. .	v.s. , sh.
1335	SO ₂ asy. Str. .	s. , b.
1270	C-O-C str. V. of ether group.	v.s. , sh.
1153	SO ₂ sy. str .	s. , b.
1100	Ar. ring v. .	w. , b.
875	C-H for :	
818	One free hydrogen atom	m. , sh.
775	Two adjacent free hydrogen atoms.	v.s. , sh.
	Three adjacent free hydrogen atoms.	v.s , sh.

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