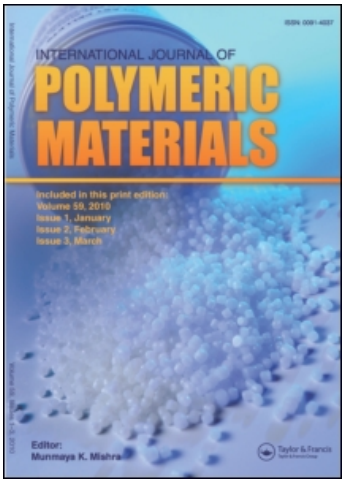

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Polyetherketones: Synthesis, Characterization and Antimicrobial Activity

Milan V. Patel[a]; Jatin N. Patel[a]; Mitul B. Dolia[a]; Rajni M. Patel[a]
[a] Department of Chemistry, Sardar Patel University, Gujarat, India

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Polyetherketones: Synthesis, Characterization and Antimicrobial Activity

Milan V. Patel
Jatin N. Patel
Mitul B. Dolia
Rajni M. Patel
Department of Chemistry, Sardar Patel University, Gujarat, India

Friedel-Crafts polyetherketones were prepared from o-chlorophenol, 1,4-phenylenedioxy diacetylchloride (1,4-PDC), chloroacetyl chloride (CAC), 1,2-dichloroethane (DCE), and dichloromethane (DCM) using anhydrous aluminium chloride ($AlCl_3$) as catalyst and carbon disulfide (CS_2) as solvent. These resins were characterized by IR spectroscopy and gel permeation chromatography. Carius method was employed to obtain the percentage of chlorine content in the resins. The kinetic parameters for the thermal behavior of the resins were evaluated from thermogravimetry (TG) using Broido method. Differential scanning calorimetry (DSC) thermograms of these resins were also obtained. All the polyetherketones were tested for their antimicrobial properties against bacteria, fungi, and yeast. It was observed that most of the polyetherketones synthesized could be used as antibacterial and antifungal agents.

Keywords: polyetherketone, thermal properties, gel permeation chromatography, antimicrobial activity

INTRODUCTION

Polyetherketones obtained by Friedel-Crafts reaction are an outstanding class of polymers. The polyetherketone blends are becoming important in several sectors of the polymer industry [1]. Surgical instruments are made from carbon-fiber reinforced poly(ether ketone)s [2]. Poly(ether ketone)s are widely used as high performance engineering thermoplastics due to their good solvent resistance, high thermo-mechanical stability, and good mechanical properties [3]. These

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Address correspondence to Rajni M. Patel, Department of Chemistry, Sardar Patel University, V. V. Nagar, 388120, Gujarat, India. E-mail: patelmv1978@indiatimes.com, patelmv1978@rediffmail.com

polymers have found many applications in aerospace, coating, electrical appliances, composite preparation, and as insulating material [4–5].

Xingdong et al. [6] prepared a series of amourphos poly(aryl ether ketone)s containing 4,4′-dihydroxydiphenyl ether by a nucleophilic route and investigated their thermal properties. Kimura and coworkers [7] prepared fluorine containing poly(ether ketone)s (PEKs) from 2,3,4,5,6-pentafluoro benzoic acid and studied the influence of electron beam irradiation on the properties of poly(ether ketone)s. They reported that thermal stability and transparency of PEKs improved significantly after irradiation.

Kenneth et al. [8] synthesized poly(aryletherketone)s from bisphenol-C and 4,4′-difluorobenzophenone, then studied their thermal stability and fire resistant properties.

Because of their antimicrobial properties [9–10], the synthesis of low molecular weight resins containing selected functional groups in gaining importance. It has been demonstrated that polymers containing chlorine are biocides [11–12]. It was therefore thought appropriate to synthesize chlorinated polyetherketones and examine their biocidal properties against bacteria (*Escherichia coli, Bacillus subtilis, and Staphylococcus citreus*), fungi (*Aspergillus niger, Sporotichum pulveralentum, and Trichoderma lignorum*), and yeast (*Candida utilis, Sacharomyces cervisiae, and Pichia stipitis*)

EXPERIMENTAL

Materials

o-chlorophenol, chloroacetyl chloride (CAC), 1,2-dichloroethane (DCE), dichloromethane (DCM), acetone, carbon disulfide (CS_2), and anhydrous aluminium chloride ($AlCl_3$) were of analytical grade and obtained from standard suppliers.

Synthesis of 1,4-phenylenedioxy diacetylchloride (1,4-PDC)

1,4-PDC (1,4-phenylenedioxy diacetylchloride) was synthesized from 1,4-PDA (1,4-phenylenedioxy diaceticacid). The product obtained was recrystallized from dry methylene chloride-hexane mixture (80:20) to give pure white needles of 1,4-PDC, having a melting point of 85°C [13].

Synthesis of Polyetherketones

o-chlorophenol, 1,4-PDC, and anhydrous $AlCl_3$ were slowly added to CS_2 one by one in a round bottom flask kept at 0°C. The reaction

was allowed to continue for an hour. After addition of appropriate reagent (i.e., CAC/DCE/DCM) (Table 1) to the mixture in the flask, the contents were heated at 60°C for 6 hours using reflux condenser. The reaction mixture was poured into H_2O:HCl (1:1) mixture with constant stirring. The slightly sticky product separated out. The product was heated on a water bath to remove CS_2. The dark brown colored solid thus obtained was dried and powdered. Brown is the characteristic color of a Friedel-Crafts product obtained from benzene and its derivatives [14]. The resin obtained was further purified using acetone as solvent and distilled water as non-solvent. The reaction schemes are depicted in Figure 1.

Characterization of Polyetherketones

The IR spectra of polyetherketones were scanned on a Perkin-Elmer 983 spectrophotometer using KBr. The percentage chlorine content of all resins was determined by Carius method [15]. Number average molecular weight ($\overline{M}n$), weight average molecular weight ($\overline{M}w$), and polydispersity ($\overline{M}w/\overline{M}n$) of polyetherketones were determined by Waters GPC instrument, equipped with 600E multisolvent delivery system, U6K manual injector series connected to ultrastyragel columns (7.6×300 mm) packed with styrene-DVB crosslinked copolymers having gel porosity of 10^3 Å–10^6 Å and molecular weight exclusion limits of 2×10^2 to 3×10^4 and 2×10^5 to 10^7, respectively. 410-RI detector and NEC powermat 386/25 data acquisition and processing unit were used for analysis. Tetrahydrofuran (THF) at 1.0 ml min^{-1} flow rate was used as a mobile phase throughout the analysis, all measurements were carried out at room temperature. The thermograms of the resins were recorded on Du Pont Model 951 thermogravimetric analyzer under static air at a heating rate of 10°C min^{-1}. The DSC data were obtained on Du Pont Model 900 thermal analyzer.

Microbial Screening

The prepared polyetherketones were tested with different microorganisms that are commonly employed for biodegradability tests. Bacterial strains (*Escherichia coli*, *Bacillus subtilis*, and *Staphylococcus citreus*), fungal strains (*Aspergillus niger*, *Sporotichum pulveralentum*, and *Trichoderma lignorum*), and yeast strains (*Candida utilis*, *Sacharomyces cervisiae*, and *Pichia stipitis*) were grown in Nutrient-broth (N-broth), Sabourand's dextrose broth, and Yeast Extract Peptone Dextrose (YEPD) medium with and without resin (control) respectively. Photometric assay method was used to

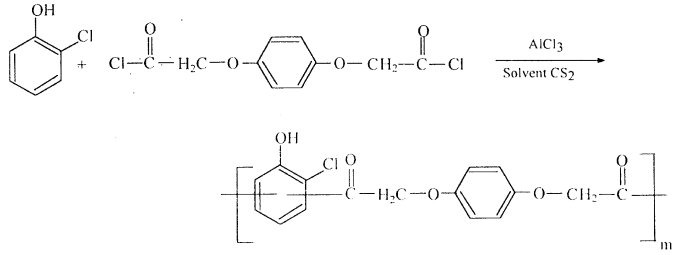
TABLE 1 Condition for the Preparation of Polyetherketones

Resin number	o-chloro phenol (mol)	1,4-PDC (mol)	CAC (mol)	DCE (mol)	DCM (mol)	$AlCl_3$ (mol)	Yield (%)	Physical state and softening range[a] (°C)	Chlorine (%)	Remarks[b]
1	0.03	0.03	—	—	—	0.06	39.9	Brown Powder 103–116	16.2	1,4-PDC + CS_2 + $AlCl_3$, was mixed and o-chloro phenol was added within 10 min.
2	0.03	0.015	0.015	—	—	0.06	35.4	Reddish brown Powder 108–119	19.0	To,1,4-PDC + CS_2 + $AlCl_3$, o-chloro phenol was added, content was kept at 0°C for 1 h and to this CAC was added
3	0.03	0.015	—	0.015	—	0.06	35.9	Dark brown Powder 99–108	18.1	To,1,4-PDC + CS_2 + $AlCl_3$, o-chloro phenol was added, content was kept at 0°C for 1 h and to this DCE was added
4	0.03	0.015	—	—	0.015	0.06	34.7	Dark brown Powder 104–117	18.3	To,1,4-PDC + CS_2 + $AlCl_3$, o-chloro phenol was added, content was kept at 0°C for 1 h and to this DCM was added

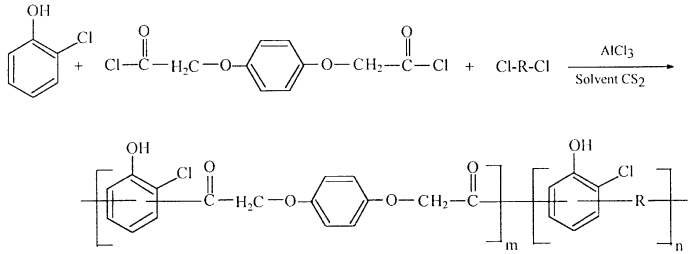
5	0.03	0.01	0.01	0.01	—	0.06	36.8	Blackish brown Powder 100–111	18.7	To,1,4-PDC + CS_2 + $AlCl_3$, o-chloro phenol was added, content was kept at 0°C for 1 h, and to this CAC was added. After 1 h, DCE was added
6	0.03	0.01	0.01	—	0.01	0.06	37.6	Blackish brown Powder 108–121	18.8	To,1,4-PDC + CS_2 + $AlCl_3$, o-chloro phenol was added, content was kept at 0°C for 1 h. and to this CAC was added. After 1 h DCM was added
7	0.03	0.01	—	0.01	0.01	0.06	38.3	Dark brown Powder 122–130	17.3	To,1,4-PDC + CS_2 + $AlCl_3$, o-chloro phenol was added, content was kept at 0°C for 1 h. and to this DCE was added. After 1 h, DCM was added

Reaction temperature: 60°C; Reaction time: 6 h; Solvent: CS_2 (25 ml); [a]From DSC thermograms; [b]The general method of preparation is already given in the text. Here specific changes for each preparation are indicated.

For resin No. 1

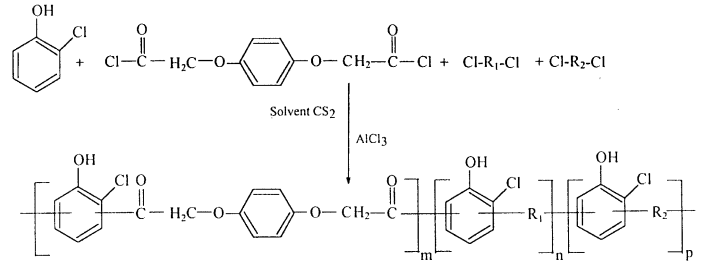


For resin No. 2, 3 & 4



For resin No. 2: R= -CH_2-C=O
For resin No. 3: R= -CH_2-CH_2-
For resin No. 4: R= -CH_2-

For resin No.5, 6 & 7



For resin No. 5: R_1=CH_2-C=O, R_2= -CH_2-CH_2-
For resin No. 6: R_1=CH_2-C=O, R_2= -CH_2-
For resin No. 7: R_1=CH_2-CH_2-, R_2= -CH_2-

FIGURE 1 Reaction scheme for the preparation of polyetherketones.

determine the toxicity effect of polyetherketones on bacteria and yeast (in terms of turbidity [16]) and on fungi (in terms of weight [17]).

The contents of each flask were incubated in a shaker at room temperature. At specific time intervals (20–48 h), the optical density was determined at 660 nm for bacterial and yeast cultures. The fungal cultures were harvested after 48 h, and the dry cell mass was determined gravimetrically. The details of the experimental procedure are reported elsewhere [18–19].

RESULTS AND DISCUSSION

The polyetherketones have been prepared under different experimental conditions. The compositions of the feed and experimental condition are presented in Table 1. All the polyetherketones are highly colored, ranging from brown to black in color. Polyetherketones are soluble in acetone, dimethyl formamide (DMF), dioxane, and so on and they soften in the range of 99–130°C. The percentage chlorine content of polyetherketones varied from 16.2 to 19.0 wt%. The number average molecular weight, weight average molecular weight, and polydispersity of resins varied from 3205 to 4535, 4530 to 8750, and 1.41 to 2.58, respectively (Table 2).

Characterization of Polyetherketones by IR Spectroscopy

The IR spectra of the resins are shown in Figure 2. All the expected characteristic group frequencies are present in these spectra. A strong absorption near 1705 cm^{-1} is observed in all of these resins. This is assigned to C=O stretching [20]. The medium strong band around 828–858 cm^{-1} in these resins may be assigned to C−H out of plane bending in phenyl ring having two adjacent hydrogen atoms [21]. The in plane C−H bending may be associated with absorption in the range 1145–1170 cm^{-1}. All the resins show strong absorption at approximately 1440 cm^{-1}, which is due to CH_2 bending in the

TABLE 2 Average Molecular Weights of Polyetherketones by GPC

Resin number	$\overline{Mn}$	$\overline{Mw}$	Polydispersity $\overline{Mw}/\overline{Mn}$
1	4535	8225	1.81
2	4210	8600	2.04
3	3205	4530	1.41
4	3665	6750	1.84
5	4050	7895	1.95
6	3385	8750	2.58
7	3525	6620	1.87

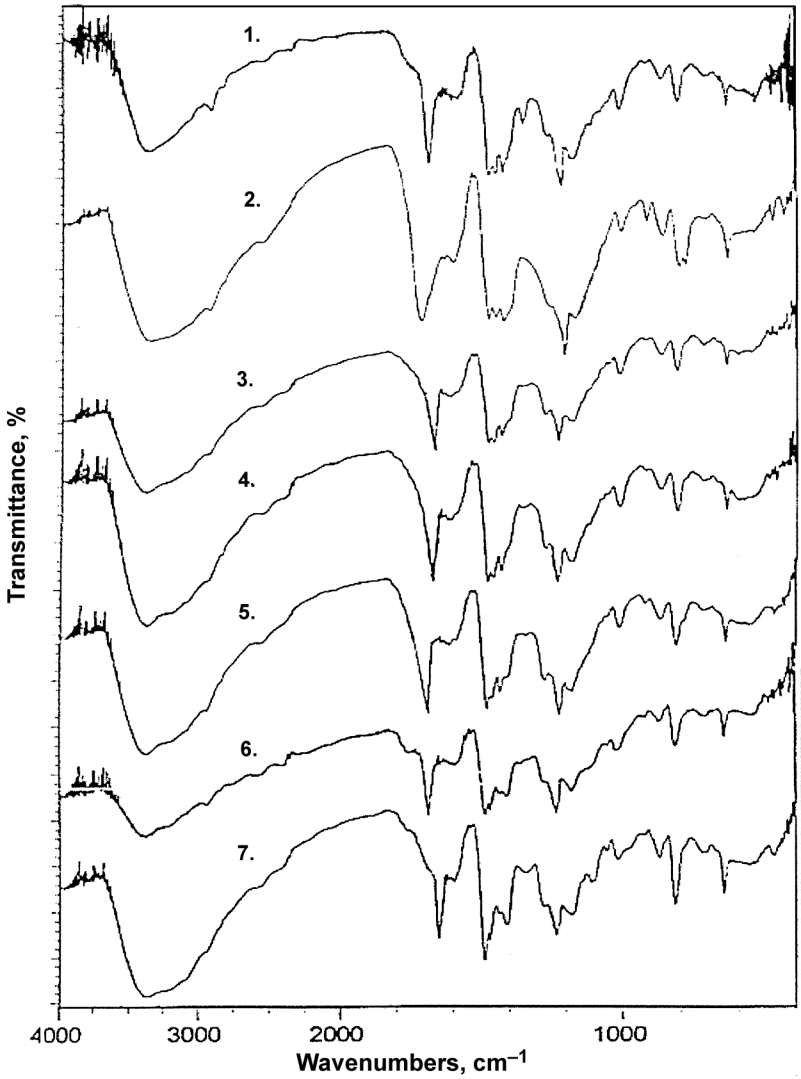


FIGURE 2 FT-IR spectra of polyetherketones.

$-CH_2-C=O$ [22] moiety. The phenyl ring vibrations cause absorptions near 1600 and 1500 cm^{-1}. The medium absorption around 1230 cm^{-1} is attributed to asymmetric C–O–C stretching, whereas the symmetric C–O–C stretching is assigned to the absorption around 1100 cm^{-1}. It is most likely that the resins also have tetra-substituted benzene ring (from p-chloro phenol) and the presence of fairly strong

absorption around 890 cm^{-1} probably lends support to this. The peak at $\sim$890 cm^{-1} is assigned to C–H out of plane bending in benzene having isolated H atom [21]. The peak in the range 3415–3430 cm^{-1} is broad due to the presence of OH stretching vibration. The C–Cl stretching is found in the range 670–690 cm^{-1} in these polymers [23].

Thermal Properties

Thermal properties of all the resins were investigated by TGA and DSC measurements. The thermal data and various kinetic parameters of thermal degradation are presented in Tables 3 and 4. It was observed that the resins show two-step decomposition. The weight loss involved in the first of the decomposition ranged from 18–32% and in second step of the decomposition it ranged from 32–96%. Most of the resins decomposed in the temperature range of 180 to 635°C. The activation energy (E_A) calculated using Broido method [24] varied from 96 to 114·K J·mol^{-1}. The values of characteristic degradation temperature and integral procedural decomposition temperature (IPDT) have been evaluated by Doyle's method [25] and are listed in Table 3. The values of heat of fusion (ΔH_f) evaluated from DSC curves, ranges between 26 to 39 J·gm^{-1} (Table 4). Resins show higher IPDT values indicating higher thermal stability.

Antimicrobial Activity

The effect of polyetherketones on the growth of microorganisms is shown in Figure 3. These results indicate that the polyetherketones

TABLE 3 Characteristic Temperatures for Thermal Degradation of Polyetherketones Evaluated from TGA

	Weight loss (%) at temperature up to							
Resin number	250°C	350°C	450°C	550°C	650°C	IPDT[a] (°C)	IDT[b] (°C)	T_S^c (°C)
1	12	19	66	90	92	452	195	440
2	16	20	24	63	86	461	180	545
3	7	18	26	64	94	536	230	525
4	6	24	28	68	96	543	240	535
5	—	23	28	64	80	538	260	530
6	5	24	32	79	87	531	225	520
7	3	25	34	78	91	527	240	510

[a]Integral procedural decomposition temperature; [b]Initial decomposition temperature; [c]Half-volatilization temperature.

TABLE 4 Kinetic Parameters for the Decomposition of Polyetherketones Obtained from TG and DSC

Resin number	Temperature range for step-1 (°C)	Weight loss for step-1 (%)	Temperature range for step-2 (°C)	Weight loss for step-2 (%)	Decomposition temperature range (°C)	ΔT	Energy of activation[a] 'Ea' ($K \cdot J \cdot mol^{-1}$)	Order of reaction 'n'	Heat of fusion[b] 'ΔH_f' ($J \cdot gm^{-1}$)
1	195–355	19	355–565	92	195–565	370	114	1	30
2	180–345	18	345–620	86	180–620	440	105	1	26
3	230–370	20	370–635	94	230–635	405	106	1	34
4	240–420	26	420–610	96	240–610	370	112	1	32
5	260–445	32	445–615	80	260–615	400	109	1	39
6	225–415	29	415–625	87	225–625	400	96	1	37
7	240–380	28	380–620	91	240–620	380	114	1	33

Rate of heating: 10°C/min; [a]Broido method; [b]From DSC thermograms.

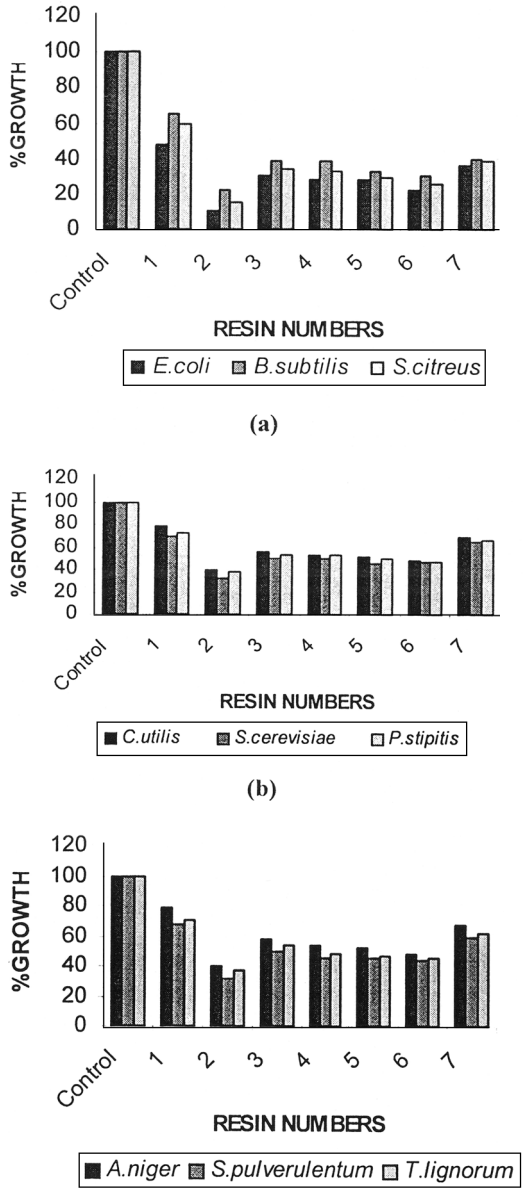


FIGURE 3 Effect of polyetherketones on percentage growth of (a) bacteria, (b) fungi, (c) yeast.

inhibit significantly the growth of microorganisms. During the period of 48 h, control culture (without resin) exhibited maximum growth. It has already been reported by earlier researchers [26–27] that chlorine-containing resins generally exhibited antimicrobial properties. All the resins investigated in the present study do contain chlorine, but there is no significant difference in the chlorine content of these resins that could account for the difference in their biocidal activity. However, it is to be noted that resin 1, which has lowest chlorine content, is the least potent antimicrobial agent and resin 2 is the most potent antimicrobial agent, having highest chlorine content.

Also, all the resins have the repeating unit $\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}CH_2}$ and resin 2 has the maximum amount of this moiety. From the feed composition it is apparent that the percentage of this moiety decreases in the resins in the following order:

$$\text{Resin 7} < \text{resin 3} \approx \text{resin 4} < \text{resin 5} \approx \text{resin 6} < \text{resin2}.$$

and interestingly the biocidal activity follows the same trend.

CONCLUSION

Seven polyetherketones were synthesized and characterized. All the resins showed two-step decomposition. For antimicrobial activity it appears that: (i) Chlorine is important for antimicrobial activity. (ii) Antimicrobial activity increases with increase in the percentage of $\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}CH_2}$ moiety.

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