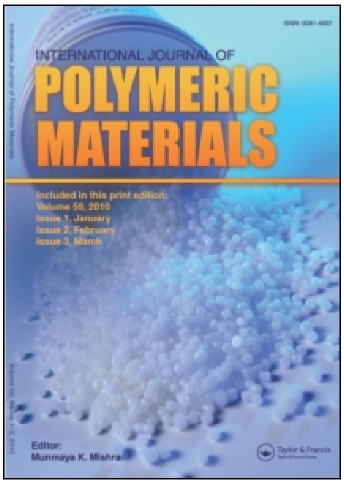


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# Synthesis, Thermal Properties and Antimicrobial Study of Some Polyetherketones

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# Synthesis, Thermal Properties and Antimicrobial Study of Some Polyetherketones

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Low molecular weight polyetherketones [PEKS] were synthesized by Friedel–Crafts reaction from *m*-methyl anisole, 1,4-phenylene-dioxydiacetyl chloride [1,4-PDC], chloroacetyl chloride [CAC], 1,2-dichloro ethane [DCE] and dichloro methane [DCM]. These polyetherketones were characterized by IR spectroscopy and Gel Permeation Chromatography. The thermal properties were studied by thermogravimetric analysis and differential scanning calorimetry. The characteristics of the decomposition reaction were evaluated by using Broido and Doyle methods. Resins tend to decompose at 200°C. Resins show significant antimicrobial activity against microorganisms such as bacteria, fungi and yeast. So they can be used as biocides for various applications.

*Keywords*: Polyetherketones; Thermal analysis; Antimicrobial activity; Friedel–Crafts reaction

## INTRODUCTION

It is possible to synthesize low molecular weight resins containing various functional groups that are gaining prominence through their various microbial and pharmacological properties [1–4]. Due to their particular characteristics, properties and variety of structures, these resins can compete with some of the known materials as far as their properties and specific applications are concerned [5–9]. With these in mind, polyetherketones were prepared and tested for their

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biocidal properties against various microorganisms such as bacteria, fungi and yeast.

## EXPERIMENTAL

### Materials

All the chemicals used for the synthesis were of laboratory grade.

### Synthesis of Polyetherketones

To a mixture of 1,4-PDC, nitrobenzene and anhydrous $AlCl_3$, *m*-methylanisole and CAC/DCE/DCM were added and kept at 0°C for one hour. After that, in some cases appropriate reagent was added (Tab. I) at a particular temperature. The reaction mixture was heated at 120°C for 4 hours. The reaction mixture was then poured into (1 : 1) 200 ml of $H_2O$ : con. HCl mixture with stirring. The tacky product was separated out. It was subjected to steam distillation to remove nitrobenzene. The dark brown coloured solid thus obtained was dried and powdered. The resin obtained was further purified using acetone as solvent and distilled water as nonsolvent. Condition for preparation of all PEKs are shown in Table I and in the reaction scheme.



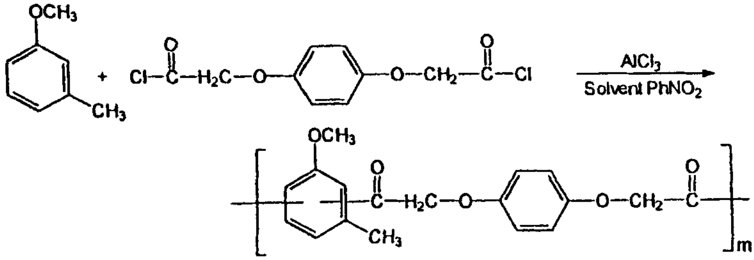
### Characterization

The experimental details for the characterization of the resins are the same as reported earlier [10, 11].

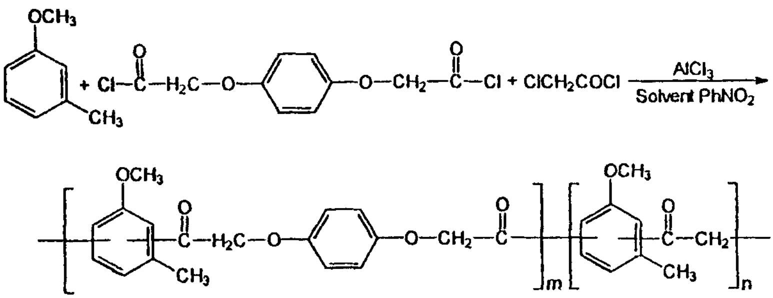
### Microbial Scanning

The polyetherketones were used to screen their microbial activity against microorganisms such as bacteria (*B. Subtilis*, *E. Coli*, *P. Fluorescens*, *S. Citreus*), fungi (*A. Niger*, *S. Pulverulentum*, *T. Lignorum*) and yeast (*C. Utilis*, *S. Cerevisiae*, *P. Stipitis*) which were grown in N. Broth, Sabourand's Dextrose Broth and YEDP medium respectively. The details of the experimental procedures are reported elsewhere [10, 11].

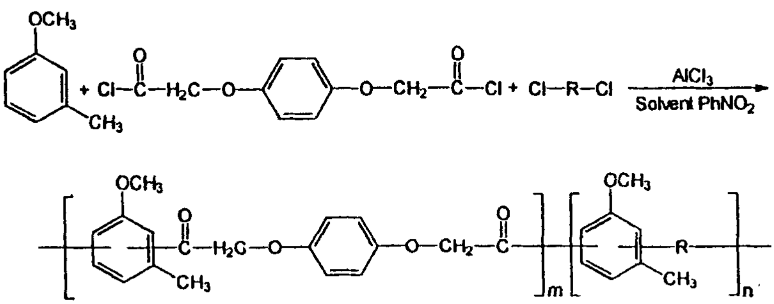
(a) For resin no. 1




(b) For resin no. 2




(c) For resin nos. 3 , 4

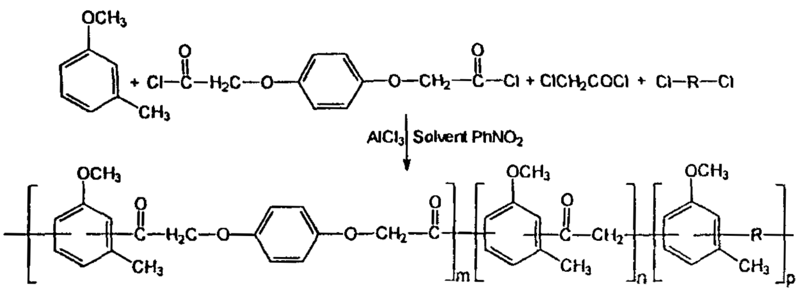



For resin no. 3 : R = $—CH_2CH_2—$

For resin no. 4 : R = $—CH_2—$

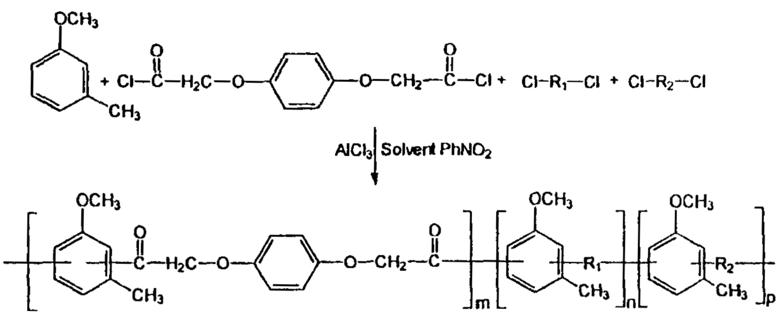
SCHEME

(d) For resin nos. 5, 6



For resin no. 5 : R = $-CH_2CH_2-$
For resin no. 6 : R = $-CH_2-$

(e) For resin no. 7



$R_1 = -CH_2CH_2-$
$R_2 = -CH_2-$

SCHEME (Continued).



## Results and Discussion

Using Friedel–Crafts reaction the polyetherketones were synthesized. They are highly coloured, ranging from brown to dark brown solids. All the resins are soluble in common organic solvents such as acetone, DMF, dioxane *etc.*

The chlorine content of the resins ranged from 5.8 to 6.4 wt% determined by Carius method [12]. The number average molecular weight ($\overline{Mn}$), weight average molecular weight ($\overline{Mw}$) and polydispersity ($\overline{Mw}/\overline{Mn}$) values of PEKs varied from 4260 to 5160, 8885

TABLE I Condition for the preparation of polyetherketones

| *Resin number* | *m-methyl-anisole (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 | 54.8 | Brown powder 136–147 | – | 1,4-PDC + $PhNO_2$ + $AlCl_3$ was mixed and *m*-methyl anisole was added within 10 min. |
| 2 | 0.03 | 0.015 | 0.015 | – | – | 0.06 | 52.0 | Reddish brown powder 125–132 | 6.4 | To, 1,4-PDC + $PhNO_2$ + $AlCl_3$, *m*-methyl anisole was added, content was kept at 60°C for 1 h. and to this CAC was added. |
| 3 | 0.03 | 0.015 | – | 0.015 | – | 0.06 | 49.8 | Dark brown powder 133–142 | 6.1 | To, 1,4-PDC + $PhNO_2$ + $AlCl_3$, *m*-methyl anisole was added, content was kept at 60°C for 1 h. and to this DCE was added. |
| 4 | 0.03 | 0.015 | – | – | 0.015 | 0.06 | 51.5 | Dark brown powder 128–139 | 6.2 | To, 1,4-PDC + $PhNO_2$ + $AlCl_3$, *m*-methyl anisole was added, content was kept at 60°C for 1 h. and to this CAC was added. After 1 h., DCE was added. |
| 5 | 0.03 | 0.01 | 0.01 | 0.01 | – | 0.06 | 52.4 | Blackish brown powder 131–144 | 6.0 | To, 1,4-PDC + $PhNO_2$ + $AlCl_3$, *m*-methyl anisole was added, content was kept at 60°C for 1 h. and to this CAC was added. After 1 h., DCM was added. |
| 6 | 0.03 | 0.01 | 0.01 | – | 0.01 | 0.06 | 53.9 | Blackish brown powder 130–140 | 5.9 | To, 1,4-PDC + $PhNO_2$ + $AlCl_3$, *m*-methyl anisole was added, content was kept at 60°C for 1 h. and to this DCM was added. |
| 7 | 0.03 | 0.01 | – | 0.01 | 0.01 | 0.06 | 50.6 | Dark brown powder 129–141 | 5.8 | To, 1,4-PDC + $PhNO_2$ + $AlCl_3$, *m*-methyl anisole was added, content was kept at 60°C for 1 h. and to this DCE was added. After 1 h., DCM was added. |

Reaction temperature: 120°C; Reaction time: 4 h; Solvent: Nitrobenzene (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.

to 12900 and 1.87 to 2.55 respectively which were measured by WATERS MAXIMA-820 GPC data processing software, (Tab. II). All the resins soften in the range of 125°C to 150°C. PEKs prepared using *m*-methyl anisole gave about 55% yield of product.

## Infrared Spectroscopy

The IR spectra of these resins show all the expected characteristic group frequencies (Tab. III) and resemble each other in all aspects. These suggest that all the PEKs are linear varying in their average molecular weights. Aromatic substitution was confirmed by the presence of C—H vibration in plane and out of plane bending at around 820 – 1200 $cm^{-1}$. Bands at 2920 – 2980 $cm^{-1}$ observed in the spectra of all the samples are attributed to —CH— stretching of alkanes. The carbonyl band appears at about 1700 $cm^{-1}$ for all the resins. A band at around 665 $cm^{-1}$ is a contribution from C—Cl. Aromatic methyl group gives two bands at around 1050 $cm^{-1}$ and 1350 $cm^{-1}$ which are symmetric stretching and asymmetric stretching respectively. The band around 1250 $cm^{-1}$ is due to $\phi$—O—$CH_2$— (ether) group presence in PEKs.

## Thermal Analysis

Tables IV and V show TG and DSC analysis of PEKs. It was observed that the resins show two step decomposition. The weight loss involved in the first of the decomposition ranged from 20 – 45% and in second step of the decomposition ranged from 45 – 99%. Most of the resins decomposed in the temperature range of 190° – 600°C.

TABLE II Average molecular weights of polyetherketones by GPC

| *Resin number* | $\overline{Mn}$ | $\overline{Mw}$ | $\overline{Mz}$ | $\overline{Mz}+1$ | *Polydispersity* $\overline{Mw}/\overline{Mn}$ | $\overline{Mz}/\overline{Mn}$ | $(\overline{Mz}+1/\overline{Mw})$ | *Mol. wt. at maximum peak height* |
|---|---|---|---|---|---|---|---|---|
| 1 | 4840 | 12345 | 30735 | 43195 | 2.55 | 2.49 | 3.5 | 5100 |
| 2 | 4590 | 10555 | 31875 | 34515 | 2.30 | 3.02 | 3.27 | 4535 |
| 3 | 4265 | 9295 | 22770 | 26950 | 2.18 | 2.45 | 2.9 | 4875 |
| 4 | 5160 | 12900 | 30830 | 42570 | 2.50 | 2.39 | 3.30 | 4395 |
| 5 | 4785 | 8945 | 22810 | 28620 | 1.87 | 2.55 | 3.2 | 5225 |
| 6 | 4680 | 8885 | 20620 | 24880 | 1.90 | 2.32 | 2.8 | 4265 |
| 7 | 4865 | 10800 | 31755 | 36070 | 2.22 | 2.94 | 3.34 | 5170 |

TABLE III Assignment of infrared frequencies of polyetherketones prepared from *m*-methylanisole

| Resin number | *CH of aromatic* Ring and $CH_2$ of bridge ($cm^{-1}$) | *Phenyl* vibration ($cm^{-1}$) | $\phi$—O—$CH_2$ | *Substituted aromatic ring* CH in plane ($cm^{-1}$) | CH out of plane ($cm^{-1}$) | *$CH_2$ bending* Scissoring ($cm^{-1}$) | Rocking of $CH_2$ of bridge ($cm^{-1}$) | *Aromatic methoxyl group* Assym. stretching ($cm^{-1}$) | Symmetric stretching ($cm^{-1}$) | C=O stretching ($cm^{-1}$) | —$H_2C$—Cl stretching ($cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2980 | 1505 | 1210 | 1170 | 845 | 1460 | 710 | 1340 | 1030 | 1700 | 640 |
| 2 | 2934 | 1513 | 1265 | 1110 | 822 | 1455 | 715 | 1352 | 1025 | 1710 | 694 |
| 3 | 2975 | 1500 | 1240 | 1130 | 830 | 1430 | 720 | 1320 | 1030 | 1690 | 650 |
| 4 | 2965 | 1510 | 1245 | 1125 | 835 | 1445 | 708 | 1335 | 1035 | 1685 | 665 |
| 5 | 2927 | 1513 | 1251 | 1180 | 822 | 1420 | 715 | 1345 | 1084 | 1690 | 655 |
| 6 | 2920 | 1533 | 1254 | 1193 | 827 | 1425 | 713 | 1360 | 1073 | 1700 | 690 |
| 7 | 2930 | 1500 | 1250 | 1180 | 830 | 1460 | 750 | 1380 | 1050 | 1695 | 660 |

TABLE IV Characteristic temperature for thermal degradation of polyetherketones evaluated from TGA

| Resin number | Weight loss (%) at temperature up to 200°C | 300°C | 400°C | 500°C | 600°C | $T_A$[a] (°C) | $IPDT$[b] (°C) | $IDT$[c] (°C) | $Ts$[d] (°C) | $Tmax$[e] (°C) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | – | 19 | 45 | 88 | 95 | 470 | 367 | 190 | 412 | 455 |
| 2 | 1.5 | 21 | 32 | 85 | 95 | 490 | 390 | 190 | 445 | 480 |
| 3 | – | 12 | 26 | 82 | 97 | 507 | 420 | 245 | 465 | 495 |
| 4 | – | 8 | 24 | 66 | 97 | 508 | 425 | 260 | 492 | 500 |
| 5 | 3 | 27 | 38 | 61 | 98 | 520 | 366 | 190 | 480 | 510 |
| 6 | – | 18 | 27 | 51 | 99 | 538 | 412 | 200 | 504 | 535 |
| 7 | – | 15 | 29 | 45 | 98 | 530 | 415 | 210 | 506 | 510 |

[a]Characteristic end-of-volatilization temperature.
[b]Integral procedural decomposition temperature.
[c]Initial decomposition temperature.
[d]Half-volatilization temperature.
[e]Maximum rate of decomposition temperature.



The activation energy calculated using Broido [13] method varied from 24.0 to 27.6 $\mathrm{Kcal \cdot mol^{-1}}$. The values of the characteristic degradation temperature have been evaluated by Doyle's [14] method and are listed in Table V. The values of heat of fusion ($\Delta H_f$) evaluated from DSC curves, range between 6.8 to 8.2 $\mathrm{cal \cdot gm^{-1}}$. Resins show higher IPDT values indicating higher thermal stability.

From the above results and discussion, it is clear that the resins exhibit moderate thermal stability. The rate of decomposition is different for all the PEKs depending upon the experimental condition, the various monomers and their concentrations.

## Microbial Activity

The effect of PEKs on the growth of microorganisms is listed in Tables VI–IX. From the data, it is revealed that the effect of polyetherketones on the growth or bacteria, fungi and yeast is not identical. Resins nos. 2, 5 and 6 show more than 50% inhibition of bacteria. All the resins are proved to be effective against *B. Subtilis E. Coli*, and *S. Citreus*. *P. Fluorescens* shows maximum growth against all the resins (Tabs. VI and VII). All the PEKs show inhibition of growth of *A. Niger*, *S. Pulverulentum* and *T. Lignorum* upto 40 hours. Resin no. 1 fails to control the growth of fungi during the experimental period (Tab. VIII). Resins nos. 2, 5 and 6 control the growth of yeast to a considerable extent (Tab. IX). From these

TABLE V Kinetic parameters for the decomposition of polyetherketones (prepared from *m*-methylanisole) found using TG and DSC

| *Resin number* | *Temperature range for Step-1 (°C)* | *Weight loss for Step-1 (°C)* | *Temperature range for Step-2 (°C)* | *Weight loss for Step-2 (°C)* | *Decomposition temperature range (°C)* | $\Delta T$ | *Energy of activation*[a] '$E_A$' ($kcal\,mol^{-1}$) | *Order of reaction* $n$ | *Heat of fusion*[b] '$\Delta H_f$' ($cal \cdot gm^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 220–550 | 95 | – | – | 220–550 | 330 | 24.0 | 1 | 7.5 |
| 2 | 190–250 | 13 | 250–550 | 95 | 190–550 | 360 | 25.7 | 1 | 7.7 |
| 3 | 245–328 | 17 | 328–560 | 97 | 245–560 | 315 | 27.2 | 1 | 6.8 |
| 4 | 260–340 | 16 | 340–550 | 97 | 260–550 | 290 | 23.8 | 1 | 6.9 |
| 5 | 190–275 | 23 | 275–560 | 98 | 190–560 | 370 | 26.8 | 1 | 7.2 |
| 6 | 210–310 | 25 | 310–560 | 99 | 210–560 | 350 | 25.5 | 1 | 8.0 |
| 7 | 230–360 | 28 | 360–570 | 98 | 230–570 | 340 | 27.6 | 1 | 8.2 |

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

TABLE VI Effect of polyetherketones (prepared from *m*-methylanisole) on the growth (%) of *B. subtilis* and *E. coli*

| *Incubation* | *B. subtilis* | | | | | | | | *E. coli* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *time* | | *Resin number*[b] | | | | | | | | *Resin number*[b] | | | | | | |
| (*h*) | *Control*[a] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | *Control*[a] | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 20 | 50 | 45 | 4 | 6 | 6 | 4 | 4 | 6 | 54 | 38 | 4 | 5 | 6 | 4 | 4 | 6 |
| 24 | 59 | 53 | 6 | 8 | 7 | 7 | 6 | 10 | 62 | 41 | 4 | 7 | 8 | 5 | 6 | 7 |
| 28 | 70 | 62 | 9 | 10 | 13 | 11 | 8 | 20 | 75 | 50 | 6 | 10 | 10 | 8 | 6 | 10 |
| 32 | 83 | 70 | 14 | 14 | 18 | 13 | 16 | 29 | 85 | 54 | 8 | 13 | 12 | 12 | 7 | 16 |
| 36 | 89 | 78 | 15 | 21 | 23 | 16 | 18 | 35 | 92 | 58 | 9 | 17 | 20 | 16 | 8 | 22 |
| 40 | 95 | 80 | 16 | 32 | 26 | 18 | 18 | 41 | 98 | 61 | 10 | 19 | 23 | 16 | 11 | 26 |
| 44 | 99 | 83 | 17 | 34 | 27 | 20 | 19 | 43 | 100 | 66 | 11 | 19 | 24 | 17 | 12 | 28 |
| 48 | 100 | 84 | 17 | 35 | 28 | 20 | 19 | 45 | 100 | 68 | 11 | 20 | 24 | 17 | 13 | 28 |

[a]Concentration of each resin was 500 ppm.
[b]Control does not contain any of the resin.

TABLE VII Effect of polyetherketones (prepared from *m*-methylanisole) on the growth (%) of *P. fluorescens* and *S. citreus*

| *Incubation* | *P. fluorescens* | | | | | | | | *S. citreus* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *time* | | *Resin number*[b] | | | | | | | | *Resin number*[b] | | | | | | |
| (*h*) | *Control*[a] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | *Control*[a] | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 20 | 63 | 51 | 7 | 12 | 11 | 9 | 9 | 14 | 59 | 48 | 3 | 5 | 7 | 4 | 4 | 9 |
| 24 | 70 | 59 | 12 | 19 | 20 | 14 | 13 | 25 | 66 | 54 | 5 | 9 | 10 | 6 | 6 | 13 |
| 28 | 79 | 67 | 25 | 31 | 36 | 30 | 28 | 45 | 79 | 60 | 9 | 16 | 19 | 11 | 8 | 20 |
| 32 | 87 | 75 | 37 | 45 | 53 | 43 | 41 | 53 | 85 | 67 | 12 | 27 | 32 | 17 | 10 | 37 |
| 36 | 95 | 86 | 49 | 49 | 64 | 51 | 50 | 74 | 91 | 76 | 14 | 36 | 48 | 21 | 17 | 49 |
| 40 | 100 | 91 | 51 | 76 | 70 | 61 | 51 | 80 | 97 | 81 | 16 | 43 | 55 | 24 | 19 | 60 |
| 44 | 100 | 95 | 52 | 82 | 76 | 63 | 59 | 88 | 100 | 84 | 18 | 48 | 57 | 26 | 21 | 61 |
| 48 | 100 | 97 | 52 | 84 | 78 | 64 | 60 | 90 | 100 | 87 | 18 | 49 | 58 | 26 | 21 | 61 |

[a]Concentration of each resin was 500 ppm.
[b]Control does not contain any of the resin.

TABLE VIII Effect of polyetherketones (prepared from *m*-methylanisole) on *A. niger*, *S. pulverulentum* and *T. lignorum*

| | *A. niger* | | | | *S. pulverulentum* | | | | *T. lignorum* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Resin number*[a] | *pH of the solution* | *Sugar utilized* (%) | *Dry weight* (*mg*) | *Growth*[b] (%) | *pH of the solution* | *Sugar utilized* (%) | *Dry weight* (*mg*) | *Growth*[b] (%) | *pH of the solution* | *Sugar utilized* (%) | *Dry weight* (*mg*) | *Growth*[b] (%) |
| Control[c] | 3.7 | 99.4 | 910 | 100 | 2.7 | 99.5 | 720 | 100 | 2.9 | 99.1 | 865 | 100 |
| 1 | 3.8 | 96.5 | 865 | 95 | 3.1 | 92.7 | 612 | 86 | 3.1 | 93.6 | 809 | 93.5 |
| 2 | 4.6 | 39.3 | 346 | 38 | 4.4 | 40.1 | 194 | 27 | 4.0 | 41.5 | 329 | 38 |
| 3 | 4.1 | 87.5 | 728 | 80 | 3.9 | 56.4 | 324 | 45 | 3.4 | 83.3 | 640 | 74 |
| 4 | 4.1 | 90.3 | 746 | 82 | 4.0 | 52.5 | 302 | 42 | 3.6 | 72.2 | 557 | 69 |
| 5 | 4.3 | 66.2 | 546 | 60 | 4.3 | 40.7 | 223 | 31 | 3.8 | 52.7 | 415 | 48 |
| 6 | 4.3 | 68.7 | 491 | 54 | 4.4 | 42.5 | 202 | 28 | 3.8 | 58.4 | 432 | 50 |
| 7 | 3.9 | 95.6 | 837 | 92 | 3.8 | 60.8 | 360 | 50 | 3.4 | 81.3 | 649 | 75 |

[a]Concentration of each resin was 500 ppm.
[b]After 40 h.
[c]Control does not contain any of the resin.

TABLE IX Effect of polyetherketones (prepared from *m*-methylanisole) on the growth(%) of *C. utilis*, *S. cerevisiae* and *P. stipitis*

| | *C. utilis* | | *S. cerevisiae* | | *P. stipitis* | |
|---|---|---|---|---|---|---|
| *Resin number*[a] | *Incubation time (h)* 24 | 48 | *Incubation time (h)* 24 | 48 | *Incubation time (h)* 24 | 48 |
| Control[b] | 60 | 100 | 52 | 100 | 49 | 100 |
| 1 | 48 | 87 | 33 | 72 | 36 | 80 |
| 2 | 9 | 20 | 2 | 6 | 5 | 29 |
| 3 | 21 | 58 | 5 | 17 | 13 | 65 |
| 4 | 17 | 45 | 4 | 14 | 13 | 68 |
| 5 | 15 | 34 | 4 | 10 | 5 | 35 |
| 6 | 13 | 32 | 3 | 8 | 9 | 40 |
| 7 | 21 | 60 | 10 | 29 | 14 | 72 |

[a]Concentration of each resin was 500 ppm.
[b]Control does not contain any of the resin.



results it is observed that the presence of chlorine in the polymers, experimental conditions and structure of the resins play an important role in controling the growth of microorganisms.

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