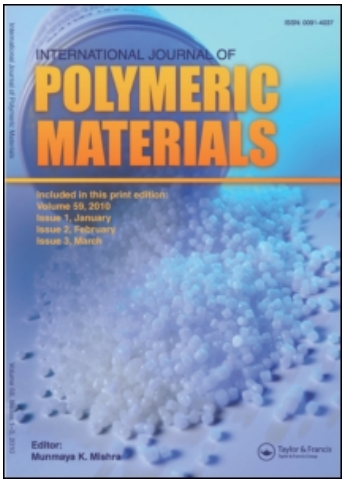

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Synthesis, Thermal Behaviour and Biological Activity of Chlorine Containing Polyketones

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Chlorine containing compounds are known to possess biological activity. This observation prompted us to synthesis Friedel–Crafts polyketones from *o*-chlorophenol, chloroacetyl chloride, 1,2-dichloroethane and dichloromethane using anhydrous aluminium chloride as catalyst and nitrobenzene ($PhNO_2$) as a solvent. The IR spectral data of these compounds indicates the presence of carbonyl and chlorine group in the resin backbone. The kinetic parameters for the thermal decomposition of the resins were evaluated from TG and DSC thermograms using methods of Broido and Doyle. Microbial study indicates the ability of the polyketone to inhibit the growth of selected species of bacteria, fungi and yeast.

Keywords: Polyketones; thermal analysis; *o*-chlorophenol; chloroacetyl chloride; biological activity

INTRODUCTION

In recent years the synthesis and development of biodegradable polymers is one of the leading frontier of research in polymer science [1–3]. Biodegradable polymers are preferred for many biomedical and agriculture applications and ecological balance as they undergo degradation by the microbes present in the environment around. During last decade extensive work has been carried out to prevent

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such degradation using certain biocides especially based on polymeric systems. With this view polyketones were prepared and tested for their biocidal properties using bacteria, fungi and yeast.

EXPERIMENTAL

Materials

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

Synthesis of Polyketones

Polyketones were prepared by using the general method described in our previous communication [4, 5] and details of experimental conditions are presented in Table I.

Characterization

The experimental details for the characterization of the resins are same as reported earlier [4, 5].

Microbial Screening

Polyketones were tested for their biological activity against bacteria (*P. fluorescens*, *B. subtilis* and *E. coli*) and yeast (*R. minuta*, *S. cerevisiae* and *P. stipitis*). The details of the experimental procedures are reported elsewhere [4, 5].

RESULTS AND DISCUSSION

A series of seven polyketones were prepared using different experimental conditions and the data are presented in Table I. The resins were soluble in common organic solvents like acetone, dioxane, dimethylformamide *etc.* All resin samples are highly coloured ranging from light brown to black and of amorphous nature. The softening point of resins varied from 98°C to 133°C and chlorine content from

TABLE I Conditions for the preparation of polyketones

Resin Number	*o-chloro-phenol* (*mol*)	*CAC* (*mol*)	*DCE* (*mol*)	*DCM* (*mol*)	*Aluminium chloride* (*mol*)	*Yield* (%)	*Physical state and softening range*[a] (°C)	*Chlorine* (%)	$\overline{Mn}$[b]	*Remarks*
1.	0.02	0.02	–	–	0.04	49	Dark brown powder 98 – 113	16.3	1765	CAC and $AlCl_3$ were mixed and *o*-chlorophenol + $PhNO_2$ was added with in 10 min.
2.	0.04	0.04	–	–	0.06	54	Brown powder 99 – 117	14.3	1821	As above
3.	0.02	0.02	–	–	0.04	51	Brown powder 105 – 121	17.3	1785	To $AlCl_3$, *o*-chlorophenol + CAC + $PhNO_2$ was added within 30 min.
4.	0.02	0.01	0.01	–	0.04	53	Light brown powder 108 – 129	17.3	1815	To $AlCl_3$ + CAC + $PhNO_2$, *o*-chlorophenol was added, content was kept at 60°C for 1h and to this DCE was added.

TABLE I (Continued)

Resin Number	*o-chloro-phenol* (*mol*)	*CAC* (*mol*)	*DCE* (*mol*)	*DCM* (*mol*)	*Aluminium chloride* (*mol*)	*Yield* (%)	*Physical state and softening range*[a] (°C)	*Chlorine* (%)	$\overline{Mn}$[b]	*Remarks*
5.	0.02	0.01	0.01	–	0.04	56	Brown powder 115–126	18.4	1750	To $AlCl_3$ + DCE + $PhNO_2$, *o*-chlorophenol was added, content was kept at 60°C for 1h and to this CAC was added.
6.	0.02	0.01	–	0.01	0.04	50	Light brown powder 120–133	17.8	1823	To $AlCl_3$ + CAC + $PhNO_2$, *o*-chlorophenol was added, content was kept at 60°C for 1h and to this DCM was added.
7.	0.02	0.01	–	0.01	0.04	51	Blackish brown powder 118–130	18.0	1840	To $AlCl_3$ + DCM + $PhNO_2$, *o*-chlorophenol was added, content was kept at 60°C for 1h and to this CAC was added.

Reaction temperature: 140°C; Reaction Time: 4 h; Solvent: Nitrobenzene (30 ml).
[a] From DSC thermogram; [b] from Vapour pressure osmometry.

TABLE II Results of TG and DSC analysis of resins

Resin number	*Decomposition temperature range* (°C)	*Weight loss (%) at temperature upto* 300 (°C)	400 (°C)	500 (°C)	600 (°C)	*Activation Energy*[a] 'E_A' ($K \cdot cal\,mol^{-1}$)	*Heat of fusion*[b] 'ΔH_f' ($Cal\,gm^{-1}$)	$IPD\dot{T}$[c] (°C)
1	180–630	16	27	49	84	21.1	6.2	395
2	215–625	13	20	40	91	28.1	6.8	450
3	250–675	05	25	37	53	26.0	6.3	470
4	230–645	10	15	27	55	27.0	5.6	445
5	185–610	16	30	58	89	20.2	5.3	410
6	190–590	18	48	85	93	19.0	6.4	370
7	205–585	14	23	49	92	18.6	6.6	395

Rate of heating: 10°C/min.
[a] Broido method. [b] From DSC thermograms. [c] Integral procedural decomposition temperature.

14% to 19%. The number average molecular weight ($\bar{M}n$) varied from 1750 to 1840.

Examination of IR spectra of all the resins reveals that all the spectra comprise important characteristic bands. Aromatic substitution was confirmed by the presence of C—H in plane and out of plane bending around $1000-1080\,cm^{-1}$ and $750-860\,cm^{-1}$ respectively. Bands around $2920\,cm^{-1}$, $2940\,cm^{-1}$ are attributed to $-CH_2-$. The carbonyl band appears at around $1700\,cm^{-1}$ and a band around $670\,cm^{-1}$ is a contribution from C—Cl.

The TG data of resins presented in Table II, reveal that the degradation of the resin commences between 200 and 250°C. The Briodo method [6] was applied to the analysis of the TG data to estimate the energy of activation (E_A) of the degradation reaction. The E_A of the resins listed in Table II range from 18 to $28\,K \cdot cal\,mole^{-1}$. The decomposition reaction of all the resins follows almost first order kinetics. The temperature characteristics of the degradation have been calculated for polyketone samples by the procedure described by Doyle [7].

The decomposition range and initial decomposition temperature for all the resins are different. This clearly indicates that the mode and rate of decomposition are different for all the resins. This is due to different experimental conditions and concentration of $AlCl_3$, *o*-chlorophenol, CAC, DCE and DCM.

Figures 1–3 furnish a comparitive account of the effect of polyketones on the growth of bacteria, fungi and yeast respectively. All the resins inhibited the growth of microorganism remarkably. Bacteria and yeast showed growth (10–29%) and (11–35%) respectively as compared with the control (*c*-without resin). Fungus showed extensive inhibition of the growth of *A. niger* and exhibited the growth of *T. longibrachiatum* and *P. chrysogenum* comparable with the control after 40 h.

From the above results, it is evident that even change in mole ratio and pattern of addition of CAC significantly changes the biological property of polyketones. However, overall significant increase in growth was observed when DCE and DCM were incorporated in particular sequence. This study enable us to identify certain condition which will allow us to synthesized polyketones as per the need and type of application.

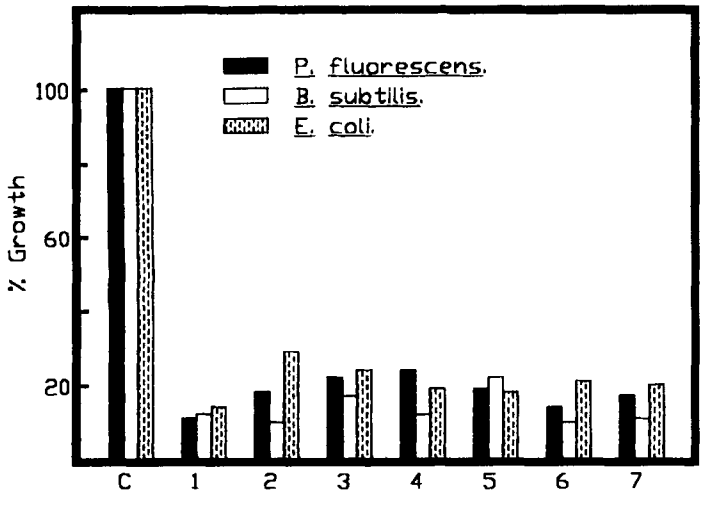

FIGURE 1 The effect of polyketones on the growth of bacteria.

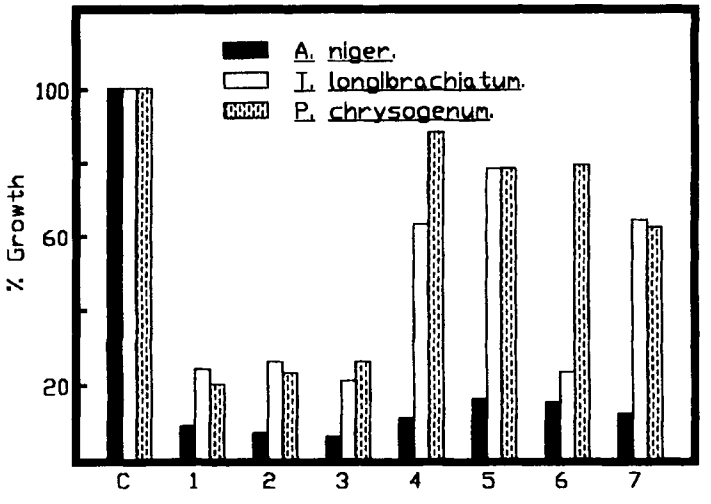

FIGURE 2 The effect of polyketones on the growth of fungi.

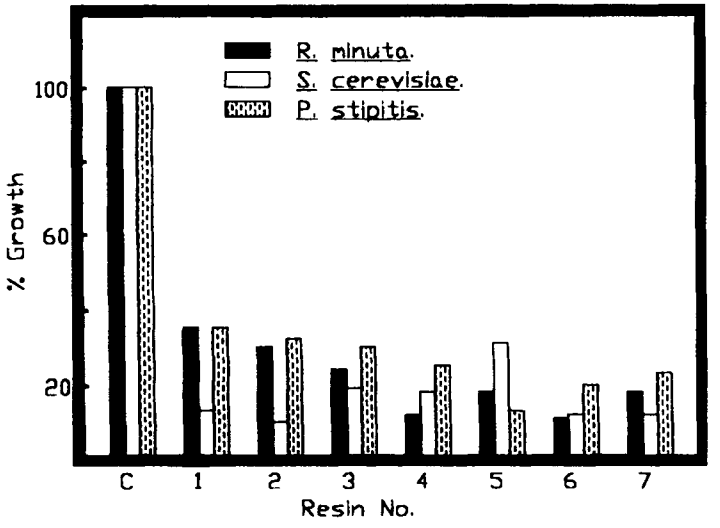

FIGURE 3 The effect of polyketones on the growth of yeast.

References

[1] Potts, J. E. (1973). Polymer and Ecological Problems (Guillet, J. E., Ed.) Plenum, 61.
[2] Eggins, H. O. W. and Mills, J. (1971). Microbial Aspects of Pollution (Sykes, G. and Skinner, F. A., Eds.) Academic, 267.
[3] Molnia, B. F. (1973). *Science*, **181**, 990.
[4] Patel, N. Z., Patel, J. N., Ray, R. M. and Patel, R. M. (1991). *Angew. Makromol. Chem.*, **192**, 103.
[5] Patel, N. Z., Patel, J. N., Ray, R. M. and Patel, R. M. (1991). *High Perf. Polym.*, **3**, 151.
[6] Broido, A. (1969). *J. Polym. Sci.*, **A-27**, 1761.
[7] Doyle, C. D. (1961). *Anal. Chem.*, **33**, 77.