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Synthesis and Antimicrobial Properties of Friedel-Crafts Polyketones

B.V. PATEL, B.T. PATEL and R.M. PATEL*
Department of Chemistry, Sardar Patel University
Vallabh Vidyanagar-388 120, India

The low molecular weight polyketones were prepared by Friedel-Crafts reaction from phenetole, chloroacetyl chloride (CAC), 1,2-dichloroethane (DCE) and dichloromethane (DCM) using anhydrous aluminium chloride as catalyst and carbon disulphide as a solvent. The polyketones thus obtained were characterized by % chlorine content, IR spectroscopy, vapour pressure osmometry, thermogravimetry and differential scanning calorimetry. All these resins were tested for their biological activity against bacteria and fungi. The results indicate that the growth of the tested organisms was inhibited by the polyketones to a considerable extent.

INTRODUCTION

Degradation of a variety of chemical compounds takes place by several microorganisms[1–5]. To prevent biological degradation of useful materials such as textiles fibres, paints, marine coatings, food packaging materials, crops, electrical insulation and pharmaceutical materials an extensive work has been carried out. With a view to identifying a class of polymeric compounds having biocidal properties, the present work describes the synthesis, characterization and biological properties of some polyketones.

EXPERIMENTAL

All the reagents used in the synthesis of polyketones were of laboratory grade.

Seven polyketones were prepared by Friedel-Crafts reaction using the general method reported in our earlier communications[6,7] and particular conditions of synthesis are as reported in Table-1.

The % chlorine content was determined by Carius method[8]. IR spectra were recorded on Perkin-Elmer 983 infrared spectrophotometer in KBr. The number average molecular weights ($\overline{M}n$) were estimated by Hewlett-Packard 302B Vapour Pressure Osmometer (VPO) using dimethylformamide (DMF) as the solvent at 70°C. Du-Pont Model 951 Thermogravimetric Analyzer (TGA) and Du-Pont Differential Scanning Calorimeter (DSC) were used to study the thermal degradation behaviour at 10°C min^{-1} heating rate in static air atmosphere.

Bacterial strains (*Bacillus subtilis* and *Pseudomonas fluorescens*), fungal strains (*Asperigllus niger* and *Trichoderma viride*) were grown in *n*-broth and Sabouraud's dextrose broth medium with and without the resins to be tested.

RESULTS AND DISCUSSION

The polyketones were prepared under different experimental conditions as presented in Table-1. Polyketones have softening points in the range from 95°C

TABLE-1

CONDITIONS FOR THE PREPARATION OF POLYKETONES[a]

Resin Number	Phenetol (mol)	CAC (mol)	DCE (mol)	DCM (mol)	$AlCl_3$ (mol)	Yield (%)	Physical state and softening range (°C)	Chlorine (%)	$\overline{Mn}^c$	Remarks[d]
1.	0.02	0.02	—	—	0.04	58	Brown powder 100–118	4.5	1700	CAC and $AlCl_3$ were mixed and phenetol was added within 10 min
2.	0.04	0.04	—	—	0.06	65	Brown powder 97–112	6.5	1650	As above
3.	0.02	0.02	—	—	0.04	60	Dark brown powder 105–123	6.1	1800	To $AlCl_3$, phenetol + CAC + CS_2 were added within 30 min
4.	0.02	0.01	0.01	—	0.04	50	Blackish brown powder 115–134	7.9	2000	To $AlCl_3$ + CAC + CS_2, phenetol was added, content was kept at 60°C for 1 h and to this DCE was added
5.	0.02	0,01	0.01	—	0.04	55	Brown powder 100–115	8.1	1700	To $AlCl_3$ + DCE + CS_2, phenetol was added, content was kept at 60°C for 1 h and to this CAC was added
6.	0.02	0.01	—	0.01	0.04	52	Dark brown powder 102–120	6.7	1750	To $AlCl_3$ + CAC + CS_2, phenetol was added, content was kept at 60°C for 1 h and to this DCM was added
7.	0.02	0.01	—	0.01	0.04	50	Blackish brown powder 120–135	7.3	2050	To $AlCl_3$ + DCM + CS_2, phenetol was added, content was kept at 60°C for 1 h and to this CAC was added

[a] Reaction temperature : 120°C; Reaction time : 4 h; Solvent : carbon disulfide (25 mL). [b] From DSC thermogram. [c] From VPO.

[d] The general method of preparation is already given in the text. Here only specific changes for each preparation are indicated.

to 135°C. The colour of the polyketones is varied from light brown to black. All are amorphous in nature and soluble in common organic solvents like carbon disulfide, acetone, DMF etc. The percentage chlorine content of these resins varied from 4 to 8. The number average molecular weights ($\overline{Mn}$) of these resins varied from 1650–2050.

The IR spectra of these resins show all the expected characteristic group frequencies and resemble each other in all aspects. The C—H in-plane and out-of-plane bending vibrations characteristic of an aromatic moiety appear in the region 1200–800 cm^{-1}. Vibration group frequencies around 2950–2825 cm^{-1}, observed in the spectra of all the samples, are attributed to —CH— stretching of alkanes. The prominent band around 1700 cm^{-1} is attributed to a carbonyl group. A band at 750 cm^{-1} observed in the spectra of all the polyketone samples is attributed to C—Cl end group[9].

Thermal characterization of all the resins was carried out by TG and DSC. The thermal data and various kinetic parameters of thermal degradation are presented in Table 2. Degradation of the resins starts between 175°C to 190°C. The actual temperature range of degradation for each resin is different, which depends upon the nature of monomers used and the experimental conditions. The activation energy (E_A) of the degradation reaction was calculated by the Briodo[10] method for each resin from TG data. The values of E_A of the resins listed in Table-2 range from 15 to 24 kcal mol^{-1}. The order of the degradation reaction of the polyketones is not identical for all the resins. The values of the characteristic degradation temperatures have been evaluated by Doyle's[11] method and are listed in Table-2 which gives characteristic end of volatilization (T_A) and integral procedural decomposition temperature (IPDT). These data reveal that the thermal stabilities of these resins are not same. The values of the heat of fusion (ΔH_f), evaluated from DSC curves, range between 5.9 to 7.8 cal gm^{-1} for all resins.

TABLE-2
RESULTS OF TG AND DSC ANALYSIS OF POLYKETONES

Resin number	Decomposition temp. range (°C)	Weight loss (%)	Energy of activation 'E_A' (kcal mol^{-1})	Order of reaction 'n'	$T_A^{(b)}$ (°C)	IPDT[c] (°C)	Heat of fusion ΔH_f (cal gm^{-1})
1.	175–615	84	22.3	1	405	325	6.2
2.	185–645	84	16.4	2	405	330	7.9
3.	175–610	90	18.6	1	390	325	5.9
4.	170–630	90	24.0	2	395	310	6.4
5.	190–620	91	14.9	1	415	345	7.2
6.	165–600	96	15.8	2	380	335	7.6
7.	190–665	83	19.3	1	410	350	7.8

[a] From Broido method. [b] Characteristic end-of-volatization temperature.
[c] Integral procedural decomposition temperature.

The data presented in Table-3 shows the effect of the polyketones on *B. subtilis* the a most common flora of soil and the *P. fluorescens* which is well

TABLE-3
EFFECT OR POLYKETONES ON THE GROWTH OF BACTERIA

Incubation time (h)	% Growth of *B. subtilis*								% Growth of *P. Fluorescens*							
	Resin number[b]								Resin number[b]							
	Control[a]	1	2	3	4	5	6	7	Control[a]	1	2	3	4	5	6	7
20	64	03	03	03	06	03	06	06	60	05	05	05	05	03	03	05
24	78	03	03	03	06	03	06	06	71	05	05	15	05	05	15	05
28	89	06	06	06	06	06	06	06	83	15	15	15	05	05	21	05
32	92	06	11	11	11	06	14	26	92	18	21	21	24	29	21	05
36	98	14	26	26	11	18	18	39	100	21	26	21	26	38	36	31
40	100	21	31	31	11	26	29	48	100	26	26	26	36	57	36	58
44	100	27	31	39	11	39	39	64	100	36	36	26	44	69	49	71
48	100	27	39	41	18	48	48	79	100	38	43	41	44	88	49	89

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

known for its wide use in the degradation of recalcitrant compounds[12, 13]. Table-4 shows the effect of polyketones on the growth of fungi. The precise and careful observation of data in Tables 3 and 4 suggests that under normal conditions, the polyketones control the growth of the tested imcro-orgranisms to a considerable extent. These results also reveal that the addition of alkyl group in the main resin chain makes them more susceptible towards biodegradation which is clearly indicated by increase in % growth of bacteria and fungi in samples 4 to 7, in which DCE/DCM were used in the resin synthesis. Further, the use of chlorine containing compounds improves biocidal properties of the polyketones. In general, the synthesized polyketones may be used as commercial biocides.

TABLE-4
ANTIFUNGAL ACTIVITY OF POLYKETONES

Resin[a] number	% Growth of *A. niger*				% Growth of *B. subtilis*			
	pH of the solution	Sugar consumed (%)	Weight of dry fungi (mg)	Growth[c] (%)	pH of the solution	Sugar consumed (%)	Weight of dry fungi (mg)	Growth[c] (%)
Control[b]	4.0	99.0	505	100.0	3.8	98.4	465	100.0
1	5.3	2.8	16	3.0	4.4	28.4	112	24
2	5.1	3.0	18	3.5	4.3	26.0	105	22
3	5.4	2.2	14	2.8	4.6	32.0	115	24
4	5.6	2.1	13	2.6	4.1	36.1	99	21
5	5.1	3.0	18	2.0	4.2	29.3	83	18
6	5.8	1.6	10	2.6	4.3	23.0	74	16
7	5.7	2.0	13	3.1	4.6	31.0	92	19

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

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