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Synthesis and Biological Activity of Polyketones-System based on *m*-Methylanisole using Nitrobenzene as Solvent

R.K PATEL, B.S RAWAL† and R.M PATEL*
Department of Chemistry, Sardar Patel University
Vallabh Vidyanagar-388 120, India

Polyketones were prepared by condensing chloroacetyl chloride/1,2-dichloroethane/dichloromethane with *m*-methylainsole in the presence of anhydrous aluminium chloride in nitrobenzene. The resin samples were characterized by an IR spectral study, measurement of their number average molecular weigh by vapour pressure osmometry, TGA and DSC. All the polymers were tested for their biological activity against bacteria (*B. Subtilis* and *P. fluorescens*). fungi (*A. niger* and *T. longibrachiatum*), and yeast (*R. minuta* and *S. cerevisiae*).

INTRODUCTION

It is well known that the degradation of a variety of chemical compounds takes place by several microorganisms[1–3]. To prevent biological degradation of textile fibres, hydrocarbon fuel systems, electrical insulations, storage tank linings, paints, crops, packaging of food items and in pharmaceutical materials tremendous work had been done during the last decade. The trend had been to prevent such biological degradation using certain biocidal polymers. Considering this aim in mind, the present study deals with the following aspects: (i) Synthesis and characterization of polyketones, and (ii) their application as microbiocides and fungicides.

EXPERIMENTAL

m-Methylanisole, chloroacetyl chloride (CAC), 1,2-dicholoroethane (DCE), dichloromethane (DCM), acetone, nitrobenzene and anhydrous $AlCl_3$ were used in the preparation of these polyketones.

Resins were prepared according to the procedure reported in our previous communication[4,5] and a particular condition is reported in Table 1. The reaction scheme is shown in Fig. 1.

Carius method[6] was used to determine chlorine content of the resins. The infra-red spectra of resins were scanned on a Perkin-Elmer Model-983 Spectrophotometer. The number average molecular weights of the resins were determined using the Hewlett-Packard Model 302B VPO at 70°C using dimethyl

†Department of Bioscience, Sardar Patel University, Vallabh Vidyanagar-388 120, India.

formamide as solvent and benzil as calibrant. The differential scanning calorimeter data (DSC) were obtained on Du Pont Model 900 thermal analyzer. The thermograms were obtained on Du Pont Model 951 thermogravimetric analyzer at a heating rate of 10°C/min under static air.

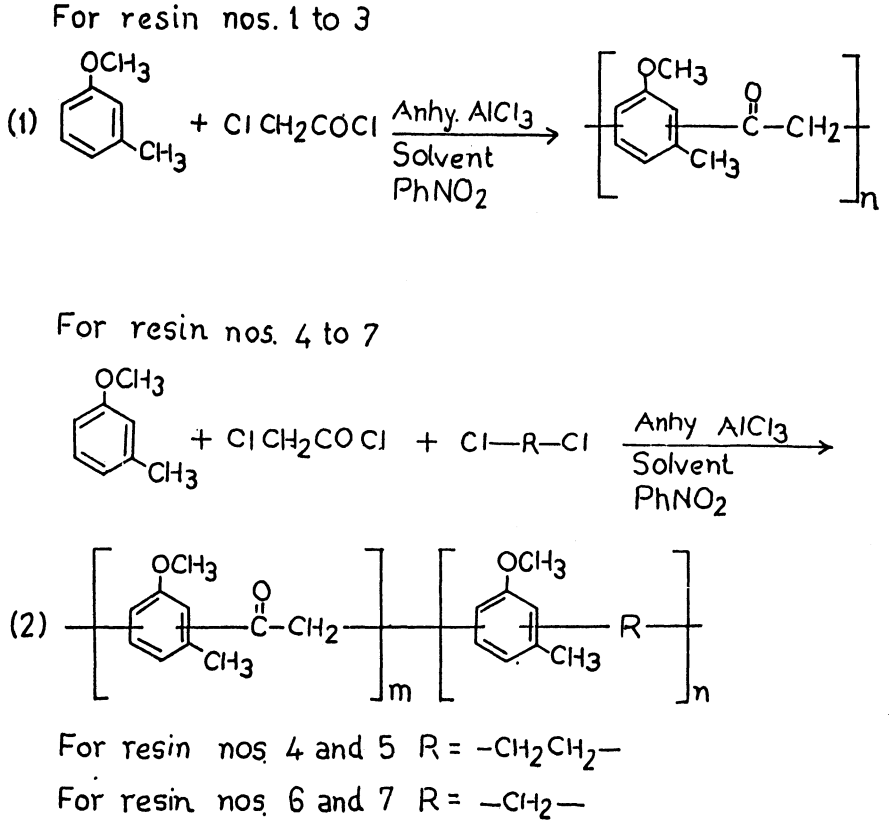

Fig. 1

Antimicrobial screeening

Bacterial strain (*Bacillus subtilis* and *Pseudomonas fluorescens*), fungal strain (*Aspergillus niger* and *Trichoderma longibrachiatum*) and yeast strain (*Rhodotorula minuta* and *Saccharomyces cerevisiae*) were grown in n-broth, Sabouraud's dextrose broth and YEDP (yeast extract peptone dextrose) medium with and without indicated resin respectively. Culture flasks were incubated on a shaker at room temperature. At specified time intervals (20-48 h), the optical density was measured for bacterial cultures. For the fungal culture, the flasks were harvested after 48 h and the dry cell mass was determined gravimetrically. For yeast culture, the optical density was determined after 24 and 48 h.

TABLE-1
CONDITIONS[a] FOR THE PREPARATION OF POLYDETONES

Resin No.	*m*-Methyl anisole (mol)	Chloroacetyl chloride (CAC) (mol)	1,2-Dichloro ethane (DCE) (mol)	Dicholoro methane (DCM) (mol)	Aluminum chloride (mol)	Yield (%)	Physical state and softening range[d] (°C)	Number average molecular weight[c] (Mn)	Chlorine (%)	Remarks[b]
1.	0.02	0.02	—	—	0.04	55	Light brown powder 100–128	2715	7.0	CAC and $AlCl_3$ were mixed and *m*-methylanisole + $PhNO_2$ was added within 10 minutes.
1.i						21	Black powder			
2.	0.04	0.04	—	—	0.06	50	Brown powder 122–138	2940	6.8	As above
2.i						22	Blackish powder			
3.	0.02	0.02	—	—	0.04	52	Dark brown powder 105–132	2809	7.4	To $AlCl_3$, m-methylanisole + CAC + $PhNO_2$ were added within 30 minutes
3.i						18	Blackish brown powder			
4.	0.02	0.01	0.01	—	0.04	48	Reddish brown powder 115–140	2980	6.4	To $AlCl_3$ + CAC + $PhNO_2$, *m*-methyl-anisole was added and contents were kept at 60°C for 1 h and to this DCE was added.
4.i						14	Blackish brown powder			

Resin No.	*m*-Methyl anisole (mol)	Chloroacetyl chloride (CAC) (mol)	1,2-Dichloro ethane (DCE) (mol)	Dicholoro methane (DCM) (mol)	Aluminum chloride (mol)	Yield (%)	Physical state and softening range[d] (°C)	Number average molecular weight[c] (Mn)	Chlorine (%)	Remarks[b]
5.	0.02	0.01	0.01	—	0.04	46	Dark brown powder	3200	5.9	To $AlCl_3$ + DCE + $PhNO_2$, *m*-methyl-anisole was added and contents were kept at 60°C for 1 h and to this CAC was added.
5.i						20	Blackish brown powder			
6.	0.02	0.01	—	0.01	0.04	45	Reddish brown powder 120–140	3010	6.6	To $AlCl_3$ + CAC + $PhNO_2$, *m*-methyl-anisole was added and contents were kept at 60°C for 1 h and to this DCM was added.
6.i						15	Black powder			
7.	0.02	0.01	—	0.01	0.04	50	Dark brown powder 123–145	3160	6.1	To $AlCl_3$ + DCM + $PhNO_2$, *m*-methyl-anisole was added and contents were kept at 60°C for 1 h and to this CAC was added.
7.i						14	Blackish brown powder			

Reaction temperature: 140°C; Reaction time: 4 h; Solvent: nitrobenzene ($PhNO_2$) (25 mL).

[d]From DSC thermogram. i, insoluble. [c]From VPO. [b]The general method of preparation is already given in the text. Here specific changes for each preparation are indicated.

RESULTS AND DISCUSSION

From the Friedel-Crafts polymerization the polyketones (1 to 7) obtained and have softening points in the range from 100°C to 165°C. The soluble resins (1 to 7) are light brown powders, while insoluble fractions (1.i to 7.i) are dark brown blackish powders. The percentage chlorine content of the soluble resins varied from 5 to 8. The number average molecular weight ($\overline{M}_n$) of resins varied from 2700 to 3200. The resins (1 to 7) produced under different experimental conditions (Table 1) were soluble in acetone and DMF.

Examination of IR spectra of all the resins exhibit all the expected characteristics. The C–H in-plane and out-of-plane bending vibrations characteristic of aromatic system appear in the region 1200–800 cm^{-1}. Vibration group frequencies around 2970–2825 cm^{-1}, observed in spectra of all the resin samples, are attributed to —CH— stretching of alkanes. The aromatic methoxy groups associated with asymmetric and symmetric stretching vibration band appear in the range 1285-1220 cm^{-1} and 1060-1020 cm^{-1}. The carbonyl bands appear around 1700 cm^{-1}. A band at 750 cm^{-1} observed in the spectra of all the polyketone samples is attributed to C—Cl end-groups[7].

The examination of thermogravimetric (TG) data of resins presented in Table 2 indicates that the degradation of the soluble resins starts between 210°C to 310°C. The degradation of the insoluble fractions commences between 300°C to 380°C. Higher thermal stability of insoluble fractions may be owing to the complexity of structure. The Broido[8] method was used to calculate the energy of activation (E_A) of the degradation reaction. The value of energies of activation of resins varing from 21 to 30 kcal-mol^{-1} depending up on the nature of reactants and reaction conditions. The heat of fusion (ΔH_f) values obtained from differential scanning calorimetry (DSC) varied from 5 to 9 J-g^{-1} for soluble resins.

Using the method described by Doyle[9] the temperature characteristics of the degradations have been calculated and are listed in Table 2 which gives characteristic end of volatilization (T_A), half volatilization (T_s) and integral procedural decomposition temperature (IPDT). These data reveal that the thermal stabilities of these resins are not same.

Table 3, 4 and 5 show antimicrobial properties of soluble resins. Results listed in Table 3 show the biological activity of polyketones on *B. subtilis*, a common soil bacterium, and *P. fluorescens*, a well known genus for biodegradation of various compounds.[10,11] The resins 3 and 5 derived from *m*-methylanisol exhibited growth of *B. subtilis* (about 22–45%) while the resins 5 and 6 exhibited growth of *P. fluorescens* (about 45–56%). This may be due to incorporation of DCE/DCM into the resins. Sequence of addition of CAC/DCE or DCM significantly affects the growth of *B. Subtilis* and *P. fluorescens.*

The results listed in Table 4 shows drastic inhibition of fungal growth *i.e.* majority of compounds are able to inhibit the fungi *A. niger* as compared to control. Inoculum added in each flask was 10%. Incorporation of DCE and DCM reduced antifungal property (resin number 5) of both *A. niger* and *T. longi-brachiatum* and concomitant reduction in sugar and pH.

TABLE-2
RESULTS OF TG AND DSC ANALYSIS OF RESINS

Resin No.	Decomposition temperture range (%)	% Weight loss at temperature upto (°C)				Energy[a] of activation, E_A kcal-mol^{-1}	Order of reaction n	T[b] (°C)	IPDT[c] (°C)	T[d] (°C)	Heat of fusion ΔH_f cal. gm^{-1}
		300	400	500	600						
1	220–575	12	25	52	78	24.6	1	463	410	495	5.9
1.i	310–620	00	14	41	76	25.3	1	591	495	525	—
2	210–555	18	28	63	80	26.1	1	561	429	475	6.8
2.i	305–640	00	11	39	78	27.2	1	587	480	530	—
3	210–560	17	27	65	77	23.6	2	578	435	470	7.4
3.i	310–635	00	18	42	63	27.5	1	637	505	540	—
4	255–570	08	19	64	79	21.2	2	589	470	480	7.8
4.i	330–650	00	07	35	77	25.7	1	595	489	535	—
5	245–585	14	25	57	78	22.5	1	571	450	485	6.5
5.i	315–630	00	13	40	76	28.4	1	594	499	520	—
6	280–640	03	12	33	64	23.7	1	638	517	550	8.4
6.i	345–675	00	05	22	54	22.8	1	660	524	590	—
7	310–590	00	12	27	70	28.1	1	646	532	545	7.9
7.i	380–685	00	01	14	50	29.9	1	673	569	595	—

[a]From Broido method.
[b]Characteristic end-of-volatilization temperature.
[c]Integral procedural decomposition temperature.
[d]Half volatilization temperature.
[e]From DSC.

TABLE-3
EFFECT OF RESIN OF THE GROWTH OF *B. Subtilis* AND *P. Fluorescens*

Incubatiion (h)	Control[a]	% Growth of *B. Subtilis* Resin number[b]							Control[a]	% Growth of *P. Fluorescens* Resin number[b]						
		1	2	3	4	5	6	7		1	2	3	4	5	6	7
20	42	2	3	2	3	3	2	4	58	3	3	3	2	4	4	4
24	47	2	5	4	3	8	2	4	65	3	3	5	4	4	8	4
28	55	3	5	4	4	14	4	6	80	3	5	5	4	14	11	6
32	67	3	5	10	4	23	4	6	97	4	5	7	6	25	19	6
36	82	3	5	17	4	26	4	6	100	4	8	10	6	34	24	6
40	100	5	5	22	4	33	8	6	100	6	8	10	6	42	24	8
44	100	5	5	22	6	38	8	6	100	6	8	10	6	49	45	8
48	100	5	5	22	6	45	8	6	100	6	8	11	6	56	45	8

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

TABLE-4
ANTIFUNGAL ACTIVITY OF RESINS AT 500 PPM CONCENTRATION ON *A. Niger* AND *T. Longibrachiatum*

Resin number	*A. Niger*				T. Longibrachiatum			
	pH of the solution	Sugar utilized	Weight of dry fungi	Growth[a]	pH of the solution	Sugar utilized	Weight of dry fungi	Growth[a]
		(%)	(mg)	(%)		(%)	(mg)	(%)
Control[b]	4.0	99.0	720	100.0	3.6	99.0	820	100.00
1.	5.6	14.3	29	4.0	5.5	17.4	31	3.7
2.	5.4	19.1	38	5.2	5.3	19.4	61	7.4
3.	4.9	22.5	75	10.4	5.5	21.2	24	2.9
4.	5.2	19.4	54	7.5	5.0	9.5	70	8.5
5.	3.8	68.5	417	57.9	3.8	60.4	415	50.6
6.	4.6	32.0	80	11.0	4.8	24.3	79	9.6
7.	5.4	17.3	42	5.8	5.1	10.6	54	6.5

[a]After 40 h.
[b]Control deos not contain any of the resin.

TABLE-5
EFFECT OF RESIN OF THE GROWTH OF *R. Minuta* AND *S. Cerevisiae*

Resin Number	Growth of *R. Minuta*		Growth of *S. Cerevisiae*	
	Incubation time (h)		Incubation time (h)	
	24	48	24	48
control[a]	62	100	67	100
1	4	6	6	6
2	3	6	4	4
3	4	9	4	6
4	6	14	8	10
5	14	37	8	21
6	8	10	6	8
7	8	8	4	8

[a]Controles does not contain any of the resin.

Filamentous yeast *R. minuta* and *S. cerevisiae* showed remarkable growth in case of resin 5 (Table 5) while the other resins showed about 15% growth. Yeast and fungi showed better growth and variation in pattern of inbibition as compared to bacteria.

Thus the above results indicate that the method of preparation and proper combination of monomer play a significant role and decide the final efficacy of the resin to be used for the purpose.

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