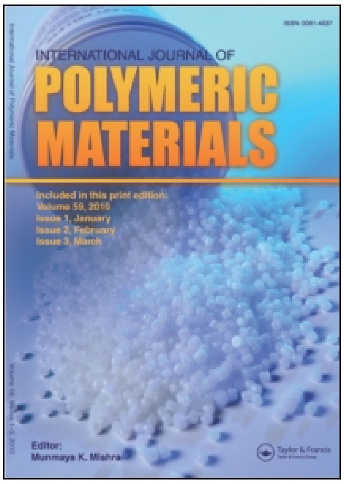

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D. I. Brahmbhatt[a]; G. B. Raolji[a]; C. N. Patel[a]; V. P. Pandya[a]
[a] Department of Chemistry, Sardar Patel University, Gujarat, India

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D. I. Brahmbhatt
G. B. Raolji
C. N. Patel,
V. P. Pandya
Department of Chemistry, Sardar Patel University, Gujarat, India

Poly(coumarin ethylenes/propylenes) were prepared by reacting 4-methyl-7-hydroxy- and 4-phenyl-7-hydroxy-coumarins with 1,2-dichloroethane and 1,3-dibromopropane in the presence of aluminum chloride under Friedel-Crafts reaction conditions by varying molar proportion of the catalyst, neat reaction and use of solvent. All poly (coumarin ethylenes/propylenes) were characterized by elemental analysis, IR spectral studies, number average molecular weight determination by non-aqueous conductometric titration, viscosity studies, and thermogravimetry.

Keywords: 4-Methyl-7-hydroxycoumarin, 4-phenyl-7-hydroxycoumarin, poly(coumarin ethylenes), poly(coumarin propylenes), Friedel Crafts Polymers

INTRODUCTION

Coumarins (2H-1-benzopyran-2-ones) form a distinct class of oxygen containing heterocycles and are widely distributed in nature. A number of naturally occurring and synthetic monomeric coumarin derivatives are used in drugs and dyes. However, compared to these monomeric derivatives little attention has been given to coumarin polymers and there are very few reports on coumarin polymers. Here it is important to note that although the reports pertaining to coumarin polymers are few, the reported coumarin polymers have varied

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Address correspondence to D. I. Brahmbhatt, Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, Gujarat, India. E-mail: drdibrahmbhatt@yahoo.co.in

properties and a wide range of applications. The coumarin polymers derived by Pechmann reaction on phenol-formaldehyde polymer are reported to have anticlotting and antihaemorrhegic properties [1]. Coumarin-N-vinyl pyrrolidine polymer reduces the blood pressure of cats [2]. Coumarin-formaldehyde polymers having phenoxy function at 3-position of coumarin moiety are reported to have antifungal properties [3]. Copolymer of coumarin with acrylonitrile is used in synthetic fiber [4]. Copolymer of vinyl coumarin with vinyl carbazole is used as an electroluminescent element [5].

Looking to the important properties of coumarin polymers [1–5] and with a view toward exploring further the field of coumarin polymers, some coumarin-based polymers like poly(coumarin methylenes) [6] and poly(coumarin ethylenes) [7] were reported from the authors' laboratory. These polymers were prepared by building up coumarin moieties on preformed salicylaldehyde-formaldehyde and salicylaldehyde-ethylene resins by Wittig reaction. In the present work such type of poly(coumarin ethylenes) (PCEs) and poly(coumarin propylenes (PCPs) have been prepared by reacting 4-methyl-7-hydroxy and 4-phenyl-7-hydroxy coumarins with 1,2-dichloroethane and 1,3-dibromopropane in the presence of aluminum chloride under Friedel–Crafts reaction conditions by varying molar proportion of the catalyst, neat reaction, and use of solvent (Scheme 1). The resultants (PCEs/PCPs) were characterized by standard techniques.

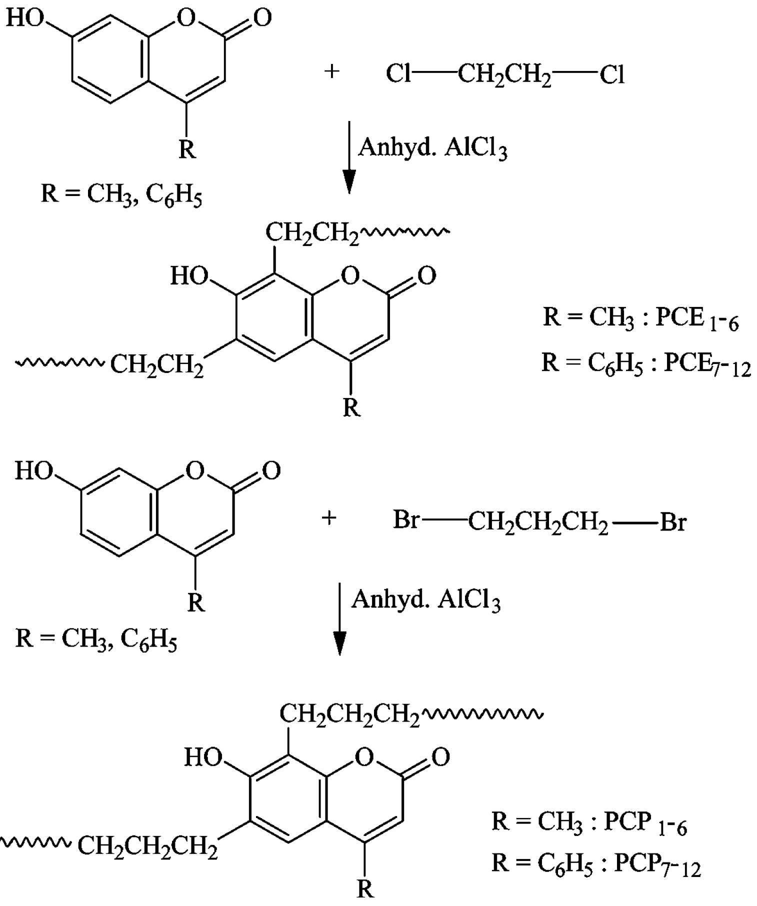
EXPERIMENTAL

Materials

The required 4-methyl-7-hydroxy- and 4-phenyl-7-hydroxy-coumarins were prepared by the literature procedures [8–9]. 1, 2-Dichloroethane and 1,3-dibromopropane used were of S.D. Fine Chemicals, Mumbai, India. All other chemicals used were of analytical or laboratory grade.

Preparation of Poly(coumarin ethylenes) ($PCE_{1\text{-}3}$/$PCE_{7\text{-}9}$)

In a 100 mL round bottom flask fitted with a reflux condenser and a guard tube were placed 4-methyl-7-hydroxy-coumarin or 4-phenyl-7-hydroxy-coumarin (0.0083 mole) and 1,2-dichloroethane (0.0166 mole). To this, a finely powdered anhydrous aluminum chloride in appropriate amount (Table 1) was then added slowly with stirring at room temperature. Then, the flask was heated in an oil bath at 150°C for 3 h. The reaction mixture was then cooled and decomposed with ice-cold 1:1 HCl-water. The polymer separated out, then filtered and washed



SCHEME 1 General polymerization procedures of poly(coumarin alkylenes).

with water and rectified spirit to remove traces of unreacted starting materials. The polymer thus obtained was dried at 100° C. Thus $PCE_{1\text{-}3}$ and $PCE_{7\text{-}9}$ were prepared. The yield and other analytical data are given in Table 1.

Preparation of Poly(coumarin ethylenes) ($PCE_{4\text{-}6}/PCE_{10\text{-}12}$)

In a 100 mL round bottom flask fitted with a reflux condenser and a guard tube were placed 4-methyl-7-hydroxy-coumarin or 4-phenyl-7-hydroxy-coumarin (0.0083 mole), 1,2-dichloroethane (0.0166 mole) and nitrobenzene (20 mL). To this, a finely powdered anhydrous aluminum chloride in appropriate amount (Table 1) was then added slowly with

TABLE 1 Characterization of PCEs and PCPs

Polymer	Amount of $AlCl_3$ (gm)	Calculated %		Found %		Intrinsic viscosity $[\eta] \times 10^2$ (in DMF at 35°C)	Mol.wt. $\overline{Mn}$	Yield %
		C	H	C	H			
PCE_1	2.22	71.3	4.9	71.4	5.0	6.9	3091	40
PCE_2	3.33	71.3	4.9	71.5	4.8	6.8	2909	48
PCE_3	4.44	71.3	4.9	71.6	5.1	6.5	2586	52
PCE^*_4	2.22	71.3	4.9	71.5	4.7	7.1	3333	45
PCE^*_5	3.33	71.3	4.9	71.3	4.8	7.0	3030	53
PCE^*_6	4.44	71.3	4.9	71.0	5.2	6.8	2868	55
PCE_7	2.22	77.3	4.5	77.3	4.4	8.6	4462	42
PCE_8	3.33	77.3	4.5	77.5	4.6	8.5	4418	49
PCE_9	4.44	77.3	4.5	77.1	4.7	8.1	3986	54
PCE^*_{10}	2.22	77.3	4.5	77.6	4.8	8.7	4673	45
PCE^*_{11}	3.33	77.3	4.5	77.5	4.3	8.4	4356	51
PCE^*_{12}	4.44	77.3	4.5	77.2	4.6	8.4	4171	57
PCP_1	2.22	72.2	5.6	72.3	5.4	8.4	3694	45
PCP_2	3.33	72.2	5.6	72.4	5.3	8.0	3413	51
PCP_3	4.44	72.2	5.6	72.0	5.5	7.4	3197	54
PCP^*_4	2.22	72.2	5.6	72.4	5.3	8.5	3888	49
PCP^*_5	3.33	72.2	5.6	72.1	5.5	8.1	3607	53
PCP^*_6	4.44	72.2	5.6	72.5	5.3	7.8	3348	58
PCP_7	2.22	77.7	5.0	77.5	5.2	9.3	5060	48
PCP_8	3.33	77.7	5.0	77.8	5.3	9.0	4587	54
PCP_9	4.44	77.7	5.0	77.4	5.1	8.6	4420	58
PCP^*_{10}	2.22	77.7	5.0	77.5	4.9	9.4	5282	50
PCP^*_{11}	3.33	77.7	5.0	77.6	5.2	9.1	4670	56
PCP^*_{12}	4.44	77.7	5.0	77.8	5.1	8.9	4643	61

*The reaction was carried out with 20 ml of Nitrobenzene.

stirring at room temperature. Then the flask was heated in an oil bath at 150°C for 3 h. The reaction mixture was then cooled and decomposed with ice-cold 1:1 HCl-water. The solution thus obtained was subjected to steam distillation to remove nitrobenzene and unreacted 1,2-dichloroethane. The polymer separated out, then filtered and washed with water and rectified spirit to remove traces of unreacted starting materials. The polymer thus obtained was dried at 100°C. Thus $PCE_{4\text{-}6}$ and $PCE_{10\text{-}12}$ were prepared. The yield and other analytical data are given in Table 1.

Preparation of Poly(coumarin propylenes) ($PCP_{1\text{-}3}$/$PCP_{7\text{-}9}$)

In a 100 mL round bottom flask fitted with a reflux condenser and a guard tube were placed 4-methyl-7-hydroxy coumarin or 4-phenyl-7-

hydroxy-coumarin (0.0083 mole) and 1,2-dibromopropane(0.0166 mole). To this a finely powdered anhydrous aluminum chloride in appropriate amount (Table 1) was then added slowly with stirring at room temperature. Then the flask was heated in an oil bath at 150°C for 3 h. The reaction mixture was then cooled and decomposed with ice-cold 1:1 HCl-water. The polymer separated out, then filtered and washed with water and rectified spirit to remove traces of unreacted starting materials. The polymer thus obtained was dried at 100°C. Thus $PCP_{1\text{-}3}$ and $PCP_{7\text{-}9}$ were prepared. The yield and other analytical data are given in Table 1.

Preparation of Poly(coumarin propylenes) ($PCP_{4\text{-}6}$/$PCP_{10\text{-}12}$)

In a 100 mL round bottom flask fitted with a reflux condenser and a guard tube, were placed 4-methyl-7-hydroxy-coumarin or 4-phenyl-7-hydroxy-coumarin (0.0083 mole), 1,2-dibromopropane (0.0166 mole) and nitrobenzene (20 mL). To this a finely powdered anhydrous aluminum chloride in appropriate amount (Table 1) was then added slowly with stirring at room temperature. Then the flask was heated in an oil bath at 150°C for 3 h. The reaction mixture was then cooled and decomposed with ice-cold 1:1 HCl-water. The solution thus obtained was subjected to steam distillation to remove nitrobenzene and unreacted 1,2-dichloroethane. The polymer separated out, then filtered and washed with water and rectified spirit to remove traces of unreacted starting materials. The polymer thus obtained was dried at 100°C. Thus $PCP_{4\text{-}6}$ and $PCP_{10\text{-}12}$ were prepared. The yield and other analytical data are given in Table 1.

Measurements

The C,H and N contents of all the PCEs and PCPs were estimated by means of a Haraeus C,H,N elemental analyzer (W. Germany). The IR spectra were taken in KBr using a Nicolett 400-D spectrophotometer. The number average molecular weight ($\overline{Mn}$) was determined by nonaqueous conductometric titration using perchloric acid in glacial acetic acid as an acid. All the PCEs and PCPs were subjected to thermogravimetric analysis (TGA) using a DuPont 950 thermogravimetric analyser in air at a heating rate of 10 K min^{-1}. The viscosity of the poly(coumarin ethylenes) and poly(coumarin propylenes) was measured in DMF at 35°C using an Ubbelohde viscometer.

RESULTS AND DISCUSSION

The formation of all polycoumarin ethylenes (PCEs) and polycoumarin propylenes (PCPs) from 4-methyl-7-hydroxy coumarin or 4-phenyl-7-hydroxy coumarin with the reaction of 1,2-dichloroethane or 1,3-dibromopropane are shown in Scheme 1.

All the PCEs and PCPs were obtained in about 40–60% yield as a reddish-brown to dark brown solid powder. They are insoluble in common organic solvents but are soluble in DMF and DMSO. The elemental analyses of all the PCEs/PCPs are consistent with their predicted structures (Scheme 1) and the results of this analysis are shown in Table 1. Examination of IR spectra of series $PCE_{1\text{-}6}$ and $PCP_{1\text{-}6}$ reveals that all the polymers of these series show characteristic bands around 2920–2940 cm^{-1} due to C–H stretching of $-CH_{2-}$ of the bridge as well as substituent methyl groups of the coumarin moietes. Each spectrum of PCEs and PCPs comprises a strong prominent band at around 1710 cm^{-1} for δ-lactone carbonyl of coumarin moiety. This indicates that the coumarin ring has remained intact throughout the polycondensation. All the polymers show broad band between 3380–3450 cm^{-1} due to O–H stretching. The polymers of the series $PCE_{7\text{-}12}$ and $PCP_{7\text{-}12}$ show the C–H out of plane deformation bands in the region 690–750 cm^{-1}. This is attributed to the five adjacent hydrogen atoms of the phenyl ring present in the coumarin nucleus at 4-position. Each spectrum of these series also shows a characteristic band at around 2920–2940 cm^{-1} due to C–H stretching of $-CH_{2-}$ of the bridge and a band around 1710 cm^{-1} for δ-lactone carbonyl of coumarin moiety.

In all the series, as the concentration of the catalyst increases, the molecular weight of polymer decreases (Table 1). It is also observed that there is an increase in molecular weight when the polymer is prepared using solvent even when the catalyst amount remains the same. These observations are in good agreement with a literature report [10] for polymers prepared by Friedal–Crafts polymerization of phenol derivatives. The molecular weight of the poly(coumarin ethylenes) (PCEs) ranges from 2586 to 4673 whereas the molecular weight of the poly(coumarin propylenes) (PCPs) ranges from 3197 to 5282. The intrinsic viscosity of all the poly(coumarin ethylenes) (PCEs) ranges from 6.5×10^{-2} to 8.7×10^{-2} dL/g and for poly(coumarin propylenes) (PCPs) varies between 7.4×10^{-2} to 9.4×10^{-2} dL/g. As the molecular weight of the polymer increases the value of intrinsic viscosity of the polymer increases, as expected (Table 1).

All the polymers degrade in a single step. All the polymers exhibited between 0.6 to 1.4% weight loss at 100°C, which may be due to some trapped solvent. The degradation of all the polymers commences at

TABLE 2 Thermogravimetric Analysis of PCEs and PCPs

Polymer	Percentage weight loss at various temperature (°C)						Energy of activation E_a (K.Cal.mol^{-1})
	100	200	300	400	500	600	
PCE_1	0.78	5.39	25.00	38.72	86.72	89.06	6.96
PCE_2	0.72	4.32	25.90	49.64	94.24	95.68	8.69
PCE_3	0.79	5.12	23.62	39.37	87.98	92.13	7.31
PCE_4	0.70	4.10	24.40	42.50	85.16	90.60	6.80
PCE_5	0.80	5.50	22.60	45.20	83.59	93.60	7.95
PCE_6	0.60	4.80	26.30	47.30	90.23	94.60	8.13
PCE_7	0.78	6.25	25.00	40.62	85.16	87.50	7.01
PCE_8	1.20	5.95	24.30	43.40	86.60	91.63	6.77
PCE_9	0.70	7.30	22.40	47.30	84.90	91.13	8.39
PCE_{10}	0.78	3.97	20.53	45.24	87.50	89.94	7.60
PCE_{11}	0.80	4.80	23.70	51.00	86.40	90.30	5.98
PCE_{12}	1.30	6.30	23.30	48.30	88.20	94.40	8.96
PCP_1	0.78	3.91	9.37	29.69	86.72	89.06	6.95
PCP_2	0.60	4.90	10.40	30.30	80.30	91.40	7.43
PCP_3	0.90	3.40	8.40	24.60	85.30	90.10	8.21
PCP_4	0.80	5.30	8.80	22.40	84.40	92.30	9.14
PCP_5	0.75	5.10	9.40	34.30	81.60	85.40	6.84
PCP_6	0.78	3.94	7.81	26.56	83.59	87.50	8.52
PCP_7	0.79	4.72	17.02	27.56	84.25	88.19	7.65
PCP_8	1.46	5.47	16.44	36.28	86.72	89.82	6.84
PCP_9	0.79	6.30	19.68	28.35	87.40	90.55	7.95
PCP_{10}	1.40	7.40	16.80	32.40	85.30	92.40	8.43
PCP_{11}	0.60	4.60	20.30	29.60	80.30	87.60	6.64
PCP_{12}	1.10	8.90	25.70	35.80	82.60	91.40	7.70

around 250°C depending on the nature of the polymer. The rate of weight loss becomes larger over the temperature range of 400–500°C and a major weight loss occurs in this range. The polymers suffer about 89–95% degradation by 600°C. Activation energy, Ea, of degradation reaction varies from 5.98 to 9.14 Kcal.mole^{-1} (Table 2).

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