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Poly(alkyl benzoate)s: preparation, properties and conversion to polyphenylenes

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Poly(alkyl benzoate)s were prepared by the coupling of alkyl dichlorobenzoates with zerovalent nickel generated *in situ* from nickel(II) bromide and characterized by ^{1}H NMR spectroscopy. While the spectra of the substituted poly(*p*-phenylene)s were complicated by the irregular distribution of substituents and the flipping of the phenylene rings, the spectra of poly(*m*-phenylene) derivatives were simple. In the spectra of poly(dodecyl-*p*-phenylene), the relative positions of the two signals due to the α-methylene group, associated with head-to-tail and head-to-head bondings of the phenylene rings, were reversed upon the introduction of the methoxycarbonyl group. The poly(alkyl benzoate)s melted under microscopic observation and thermally decomposed in two stages. The decomposition temperature ranged from 380 to 460°C for the first stage and from 550 to 590°C for the second stage. These findings indicated that these polymers were soluble, fusible and thermally stable. The poly(alkyl benzoate)s were hydrolysed and decarboxylated to the corresponding polyphenylenes. Although the substituted poly(*p*-phenylene)s were easily converted to polyphenylenes, the poly(*m*-phenylene) homologues were resistant to hydrolysis.

(Keywords: poly(alkyl benzoate)s; poly(*m*-phenylene); poly(dodecyl *p*-phenylene))

INTRODUCTION

Poly(*p*-phenylene) (PPP) is one of the simplest and most promising polymers. It is a linear polymer consisting only of benzene rings, containing no heteroatoms, and is extremely resistant to thermal degradation. Van Kerckhoven *et al.* prepared PPP by the Diels-Alder reaction of 5,5′-*p*-phenylenebis-2-pyrone with *p*-diethynylbenzene and showed that the PPP lost only 10% of its weight at 650°C and 20% at 800°C under a nitrogen atmosphere[1].

PPP is promising not only for its thermal stability, but also for its high electrical conductivity and other properties related to the conjugated main chains. Schacklette *et al.* showed that the electrical conductivity of PPP increased to $5 \times 10^2\,\mathrm{S\,cm^{-1}}$ upon doping with arsenic pentafluoride and $10\,\mathrm{S\,cm^{-1}}$ upon doping with potassium at the early stage of studies on conducting polymers[2]. Recently, Goldenberg *et al.* showed that PPP could be cycled between oxidized and neutral states in the presence of trifluoromethanesulfonic acid[3,4]. Because structural defects markedly reduce electronic properties, it is extremely important to prepare polymers which have highly regular structures.

Busch first reported the preparation of the hexadecamer in 1936[5]. Subsequent work by Kovacic showed that PPP could be prepared by the oxidation of benzene using copper(II) chloride in the presence of aluminium chloride[6]. Kobryanskii and Arnautov also prepared PPP by the oxidation of benzene. In this case however, the use of copper(II) chloride in a mixture of butylpyridinium chloride and aluminium chloride yielded high quality PPP[7]. A serious limitation of all these procedures however, was that the intractable polymer was produced in the form of a powder.

A preferable preparative method is to use a soluble precursor route in which the precursor film can be processed and pyrolysed to PPP. In 1959, Marvel and Hartzel demonstrated that 1,4-addition polymerization of cyclohexadiene followed by dehydrogenation of the resulting poly(cyclohexadiene) would yield PPP[8]. Douglas adapted this method and proposed an improved route via a soluble precursor. This approach gave PPP with the expected structure and high molecular weight upon pyrolysis[9].

As for substituted PPP, Wegner stressed that palladium-catalysed coupling of boric acid with bromide

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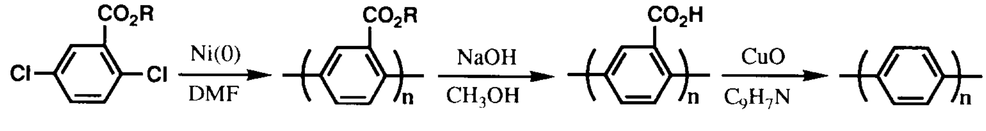


$R = CH_3$, MCPB PMPP PCPP PPP
$R = C_2H_5$, ECPB PEPP

Scheme 1

according to the Suzuki reaction was a useful route to high quality alkylated and alkoxylated PPP[10–12]. Wallow and Novak prepared carboxylated PPP in the same way[13], and this was the first water-soluble PPP. Child and Reynolds prepared sulfonatopropoxy-substituted PPP, which was also soluble in water and self-doped with its own sulfonic acid[14]. On the other hand, John and Tour prepared substituted PPPs by thermal polymerization of enediynes[15]. These polymers were soluble in organic solvents and stable up to 400°C. It can thus be seen that it is still of current importance to find a route to PPP and its substituted homologues with well-defined structure. As for poly(*m*-phenylene) (PMP) and its substituted homologues, no systematic studies have been carried out. Yamamoto *et al.* briefly reported the preparation of PMP by the Grignard coupling of 1,3-dichlorobenzene[16].

The carbonyl-substituted dihalobenzenes were impossible to polymerize. In 1986 however, Colon and Kelsey showed that carbonyl-substituted halobenzenes could be coupled by zerovalent nickel generated *in situ* from nickel(II) chloride[17]. It was shown in the previous paper that poly[2-(methoxycarbonyl)phenylene-1,4-diyl] (PMPP) could be prepared by the dehalogenative polymerization of methyl dichlorobenzoate according to this procedure and that it was a precursor to high quality PPP[18]. In the present paper, several kinds of substituted PPP and PMP are prepared and characterized by ^1H n.m.r. They are soluble and show high thermal resistivity. These polymers were hydrolysed and decarboxylated to the corresponding polyphenylenes.

RESULTS AND DISCUSSION

Preparation of poly(p-phenylene)s

Poly(*p*-phenylene)s were prepared according to *Scheme 1*. Methyl 2,5-dichlorobenzoate (MCPB) and ethyl 2,5-dichlorobenzoate (ECPB) were polymerized in pyridine, *N,N*-dibutylformamide (DBF), and *N,N*-dimethylformamide (DMF). The results are summarized in *Table 1*. DMF gave high yield and high degree of polymerization (*DP*). Pyridine gave a narrow molecular weight distribution.

Table 1 Polymerization of MCPB and ECPB

Run	Monomer	Solvent	Yield (%)	*DP*	M_w/M_n
1	MCPB	Pyridine	33	67	1.3
2	MCPB	DBF	36	52	1.5
3	MCPB	DMF/pyridine (2:1)	30	55	1.2
4	MCPB	DMF	85	104	2.1
5	ECPB	DMF	40	60	1.5

Polymerization temperature = 80°C

The ^1H n.m.r. spectrum of poly[2-ethoxycarbonyl)-phenylene-1,4-diyl] (PEPP) is presented in *Figure 1*. The aromatic part (7.2–8.4 ppm) was very similar to that of PMPP. The signals due to the alkoxy methylene group occurred at 4.1–4.5 ppm and the signals due to the methyl group at 1.0–1.5 ppm. Complicated features of these signals were attributed to the combination of head-to-tail and head-to-head bondings and the flipping of the phenylene rings. The small signals at low field of the methylene and methyl groups are probably associated with the terminal units. This spectrum is compatible with those of PMPP previously reported[18,19].

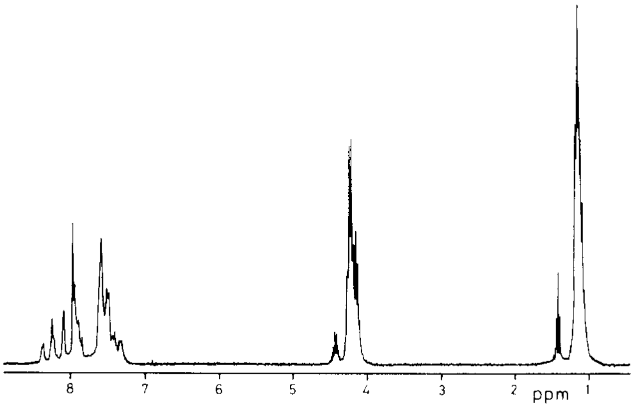


Figure 1 ^1H n.m.r. spectrum of PMPP in $CDCl_3$

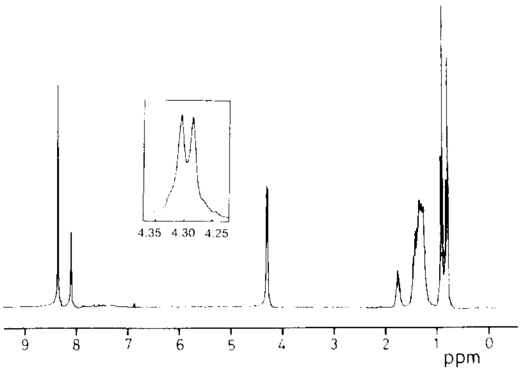
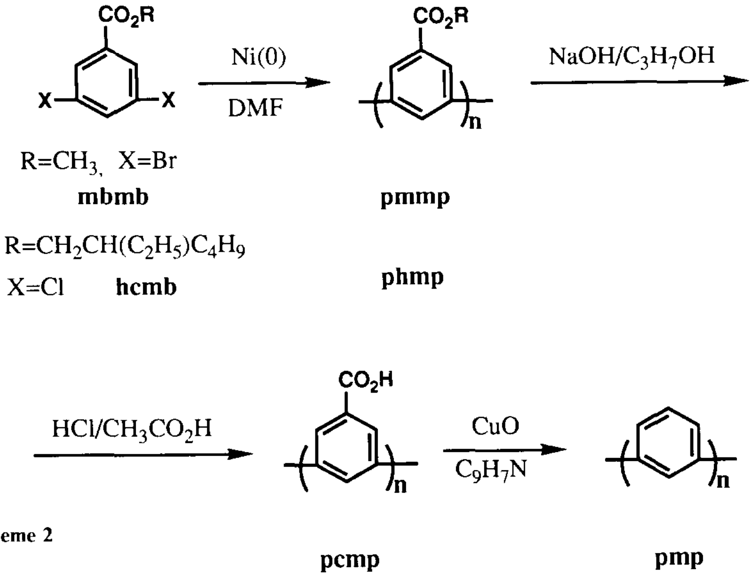


Figure 2 ^1H n.m.r. spectrum of PHMP in $CDCl_3$. Inset: the signal due to the alkoxy methylene group

polymerization.



Scheme 2

*Preparation of poly(*m*-phenylene)s*

Poly(*m*-phenylene)s were prepared according to *Scheme 2*. Poly[5-(2-ethylhexyloxycarbonyl)phenylene-1,3-diyl] (PHMP) was prepared by dehalogenative coupling of 2-ethylhexyl 3,5-dichlorobenzoate (HCMB) in the presence of Ni(0) produced *in situ* according to Colon's procedure[17]. The polymerization was conducted in DMF at 40 and 80°C for 24 h. During the course of polymerization, the polymer precipitated from the polymerization mixture and formed lumps, which interfered with stirring seriously. The yield and degree of polymerization are clearly lower than those of PMPP[18].

PHMP is a white solid that is soluble in chloroform but not in dimethyl sulfoxide or propyl alcohol. In the i.r. spectrum of PHMP, the strong aliphatic C–H stretching bands occur at 2850, 2940 and 2952 cm^{-1}. The intensive band at 1727 cm^{-1} is due to the carbonyl group of the ester. The C–O stretching band occurs at 1231 cm^{-1}. The bands at 762 and 705 cm^{-1} are due to the out-of-plane C–H deformation of the benzene ring. The band at 1155 cm^{-1} due to C–Cl stretching which is present in the spectrum of the monomer disappears upon polymerization.

Figure 2 shows the ^1H n.m.r. spectrum of polymer PHMP in $CDCl_3$ at room temperature. Two triplet signals due to two methyl groups are seen at 0.75–0.85 and 0.85–1.0 ppm and methylene signals occur at 1.16–1.5 ppm. A multiplet signal due to the methine proton is seen at 1.7–1.83 ppm and a doublet due to the alkoxy methylene group at 4.3 ppm. In the aromatic region, two signals occurred at 8.1 and 8.3 ppm due to protons at the 4 position and the 2 and 6 positions, respectively. Because there is only one ring bonding mode and no flipping of *m*-phenylene rings, the signals due to the alkoxymethylene and aromatic proton are simple. It is evident that PHMP has a well-defined structure.

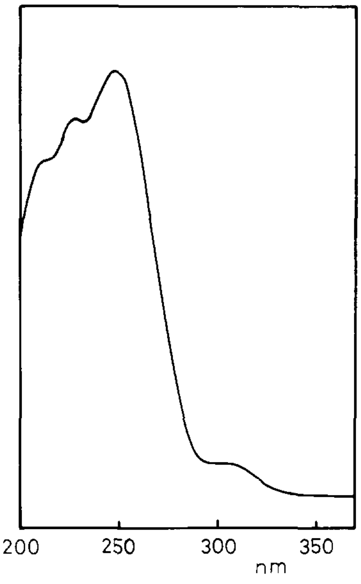


Figure 3 U.v. spectrum of a PHMP film

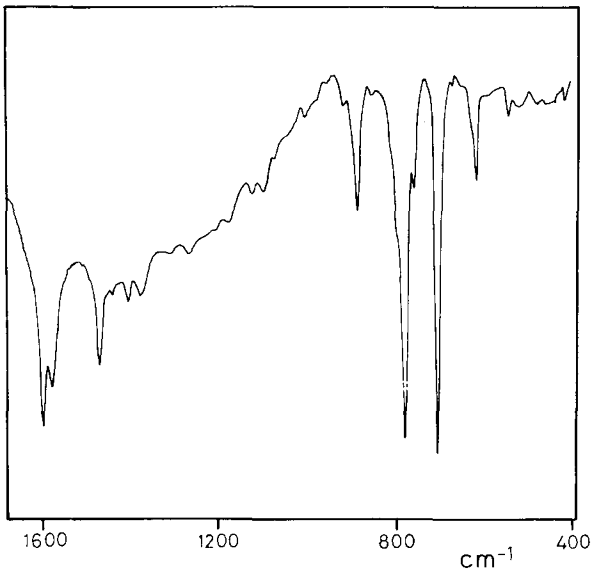
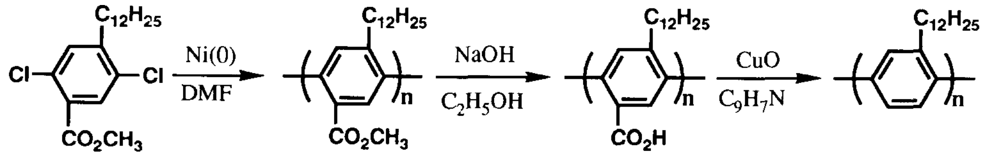


Figure 4 I.r. spectrum of PMP in KBr disc



mdcpb pmdpp pcdpp pdpp

Scheme 3

A thin film of PHMP was cast on a quartz plate from a chloroform solution. The u.v. absorption spectrum is presented in *Figure 3.* Four peaks were observed at 210, 228, 246 and 310 nm. No peaks occurred in the visible region, indicating that there is no appreciable conjugation between the benzene rings.

Poly[5-(methoxycarbonyl)phenylene-1,3-diyl] (PMMP) was prepared in a similar way. Since PMMP was insoluble in benzene and turbid in chloroform or tetrahydrofuran (THF), it is hard to characterize by g.p.c. and n.m.r. It is only soluble in trifluoromethanesulfonic acid to make a black solution.

Although PMPP was easily hydrolysed, PHMP was resistant to hydrolysis. Refluxing with 20% methanolic sodium hydroxide resulted in partial hydrolysis. For this reason, hydrolysis was carried out in a higher-boiling solvent, followed by acidic hydrolysis. Poly(5-carboxyphenylene-1,3-diyl) (PCMP) was obtained as a white powder. In the i.r. spectrum of PCMP, the bands due to the alkyl group disappeared upon hydrolysis. PMMP was hydrolysed in the same way.

PCMP was also found to be resistant to decarboxylation and thus, prolonged heating with copper(II) oxide was necessary. The i.r. spectrum of PMP is shown in *Figure 4.* It is more complicated than that of PPP. This spectrum is similar to the previously reported one of PMP produced by the Grignard coupling of 1,3-dichlorobenzene[16]. However, the black–brown colour of PMP was quite different from the previously reported white.

*Preparation of poly(3-dodecyl-*p*-phenylene) (PDPP)*

Starting with 2,5-dichlorobenzoic acid, methyl 2,5-dichloro-4-dodecylbenzoate (MDCPB) was prepared via a four-step reaction. The i.r. and ^1H n.m.r. spectra were compatible with the structure of MDCPB.

Methyl 2,5-dichloro-4-dodecylbenzoate (MDCPB) was polymerized in DMF under the effect of zerovalent nickel produced *in situ* in a similar way to HCMB. Poly[2-dodecyl-5-(methoxycarbonyl)phenylene-1,4-diyl] (PMDPP) was obtained as a yellow powder which was soluble in chloroform, THF and toluene but not in acetic acid, acetone or methanol. The *DP* of PMDPP was 13–22.

PMDPP was hydrolysed in a sodium hydroxide solution in ethanol. Although part of the solid polymer remained undissolved, the hydrolysis took place to produce white poly(2-carboxy-5-dodecylphenylene-1,4-diyl) (PCDPP). When the recovered PCDPP was washed with methanol, 30% of it was extracted and 70% remained. Both extracted and unextracted PCDPP showed the same i.r. spectra but the extracted part was a low molecular weight paste after evaporation of methanol. Thus, starting with PMDPP with *DP* of 13 (run 7 in *Table 2*), PDPP with *DP* of 22 was obtained (*Scheme 3*).

Figure 5 shows the ^1H n.m.r. spectra of PMDPP and PDPP. In the spectrum of PMDPP, signals due to the methoxy group arose at 3.91, 3.69, 3.61 and 3.59 ppm. The signal at 3.91 ppm would be due to the methoxy group at the termini. Two signals due to the α-methylene group occurred at 2.70 and 2.52 ppm and their ratio was 20 : 80. In the spectrum of PDPP, these signals occurred at 2.73 and 2.46 ppm and their ratio was 81 : 19. These two signals are assignable to head-to-tail and head-to-head bondings of the phenylene units. In the spectra of poly(3-alkylthiophene), the low field signal was assigned to head-to-tail bonding and the high field signal to head-to-head bonding[20,21]. This assignment can be confirmed from the ^1H n.m.r. spectra of poly(3,3′-dihexyl-2,2′-bithiophene) which is composed only of head-to-head bonding[22] and regioregular poly(3-hexylthiophene) which is composed only of head-to-tail bonding[23]. In the spectra of the copolymer of *p*-phenylene and 2,5-dihexyl-*p*-phenylene units, the intensity of the high field signal increases with increasing concentration of the 2,5-dihexyl-*p*-phenylene unit[24]. It is reasonable to assume that the signal due to the head-to-head bonding resonates at high field in the spectrum of PDPP. Accordingly, in the

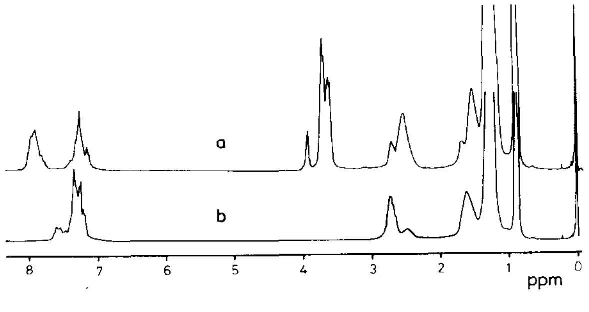


Figure 5 ^1H n.m.r. spectrum: (a) PMDPP; (b) PDPP

Table 2 Polymerization of various monomers

Run	Monomer	Temp. (°C)	Yield (%)	*DP*	M_w/M_n
1	MBMB	55	55	–	–
2	MBMB	70	57	–	–
3	HCMB	40	35	47	1.2
4	HCMB	80	41	55	1.3
5	MDCPB	100	91	22	3.0
6	MDCPB	115	75	14	1.5
7	MDCPB	100	95	13	1.9

Solvent = DMF

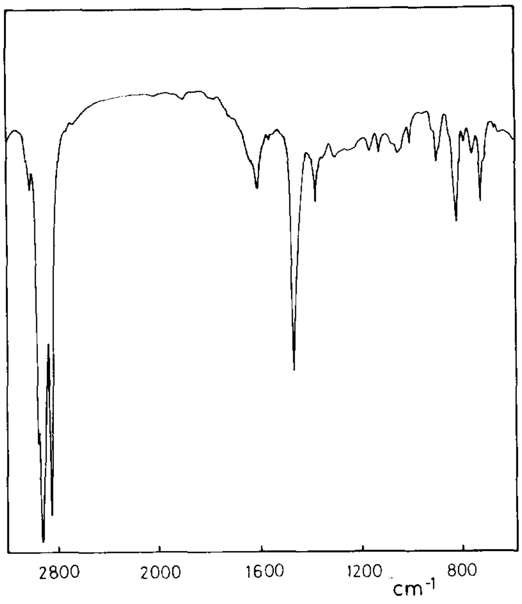


Figure 6 I.r. spectrum of PDPP in KBr disc

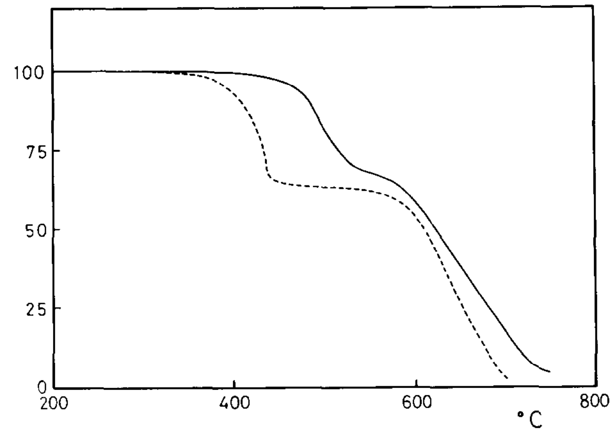


Figure 7 T.g.a. curves: (——) PMPP; (- - - -) PEPP

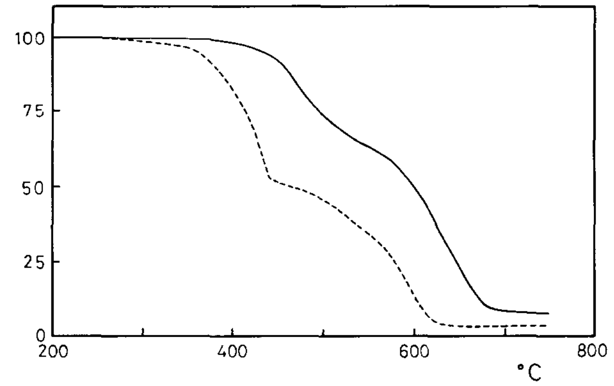


Figure 8 T.g.a. curves: (——) PMMP; (- - - -) PHMP

spectrum of PMDPP the signal from the head-to-head bonding occurred in the low field. These findings indicate that the head-to-tail sequence is rich in these polymers but that the relative positions of the two signals are reversed by the introduction of the methoxycarbonyl group. In the ^{1}H n.m.r. spectrum of PCDPP in pyridine, these signals shifted to around 2.95 and 2.80 ppm. Although their separation is not large enough to discuss quantitatively, the signal to low field is clearly stronger, similar to the spectrum of PDPP.

Table 3 Thermal properties of poly(alkyl benzoate)s

Polymer	Decomposition temperature First stage (°C)	 Second stage (°C)	Melting point (°C)
PMPP	464	586	310–313
PEPP	398	588	270–276
PMMP	441	585	300–305
PHMP	382	545	197–205

On the other hand, in the ^{1}H n.m.r. spectrum of the oligomer prepared by the coupling of 2,5-dichloro-1-octylbenzene in the same way, the above signals occurred at 2.76 and 2.50 ppm and their ratio was 28 : 72. The methoxycarbonyl group increased the content of head-to-tail bonding.

Figure 6 shows the i.r. spectrum of PDPP. This system is very similar to the spectrum of the above-mentioned oligomer. The present spectrum showed a stronger band at 722 cm^{-1} due to the methylene groups and a weaker band at 1004 cm^{-1}.

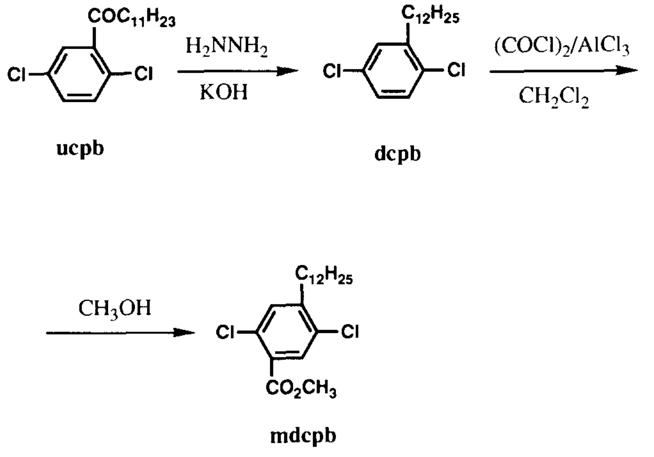
Thermal properties

The thermogravimetrical analysis (t.g.a.) curves of poly(alkyl benzoate)s are presented in *Figures 7* and *8*. The decomposition temperatures and melting points are summarized in *Table 3*. All four polymers were thermally stable and decomposed in two stages. The first stage would be associated with the scission of the side chains and the second stage with main chain scission. PMPP was the most stable among these polymers and started decomposing at 464°C for the first stage and at 588°C for the second stage. PEPP started decomposing below 400°C, much lower than PMPP, but at almost the same temperature for the second stage as PMPP. PMMP started decomposing at 441°C for the first stage and at 585°C for the second stage. The corresponding temperatures for PHMP were 382°C and 544°C, respectively. This behaviour indicated that substituted poly(*p*-phenylene)s were more resistant than *meta* homologues and that the long alkyl group markedly decreased the decomposition temperature for the first stage but not so markedly for the second stage. All these polymers melted under microscopic observation. The melting points ranged from 200 to 300°C. Long alkyl groups decreased the melting points. These findings indicate that poly(alkyl benzoate)s were fusible and thermally stable.

EXPERIMENTAL

Synthesis of monomer

Synthesis of MDCPB. A mixture of 1,4-dichloro-2-dodecanoylbenzene (UCPB) (24 g, 7.3×10^{-2} mol) hydrazine hydrate (24 ml, 60%) and ethylene glycol (290 ml) was allowed to react at 210°C for 5 h. After cooling, potassium hydroxide (15.4 g, 2.34×10^{-1} mol) was added and heated at 160°C for 2.5 h. The reaction mixture was poured into water and extracted with diisopropyl ether. Organic layers were washed with water



Scheme 4

and dried over magnesium sulfate. After solvents were distilled, the residue was purified on a silica gel column with n-hexane as eluent, 1,4-Dichloro-2-dodecylbenzene (DCPB) was obtained as a colourless oil. The yield was 16.1 g (5.1×10^{-2} mol, 70%).

^{1}H n.m.r. ($CDCl_3$): 0.88 (3H, t), 1.27 (18H, m), 1.52 (2H, m), 2.68 (2H, t), and three unseparated peaks centred at 7.21 ppm (3H, s).

I.r. (neat): 720(w), 810(s), 872(m), 883(sh), 938(vw), 1042(m), 1074(sh), 1094(s), 1134(w), 1197(w), 1263(vw), 1302(vw), 1355(vw), 1377(w), 1393(m), 1467(s), 1560(w), 1588(m), 2854(s), 2928(s), 2960(sh), 3030(sh), and 3080 cm^{-1}(sh).

After a reaction vessel was charged with anhydrous aluminium chloride (72.3 g, 5.42×10^{-1} mol) and dry methylene chloride (850 ml), oxalyl chloride (206 g, 1.62 mol) was added dropwise at room temperature. Subsequently, DCPB (170 g, 5.4×10^{-1} mol) was also added dropwise and stirred at room temperature for 5 h. The reaction mixture was then poured into 2.5 l of methanol while cooling and was stirred for 3 h at room temperature. It was then concentrated, poured into water and extracted with methylene chloride. The organic layers were collected, washed with water and dried over magnesium sulfate. After the solvent was distilled, the purification of the residue on a silica gel column with n-hexane/ethyl acetate (20/1) gave 23.5 g of a crude product which was purified again on a silica gel column with n-hexane/ethyl acetate (100/1) and recrystallized from methanol twice. Thus, pure MDCPB was obtained (*Scheme 4*). The yield was 7.5 g (3.7%).

^{1}H n.m.r. ($CDCl_3$): 0.87(3H, t), 1.25(18H, m), 1.59(2H, m), 2.76(2H, t), 3.92(3H, s), 7.30(1H, s), 7.85(1H, s).

I.r. (KBr): 553(m), 658(m), 693(w), 722(m), 781(m), 820(w), 866(m), 914(m), 941(w), 975(m), 1078(s), 1135(s), 1200(m), 1261(s), 1281(s), 1299(s), 1313(m), 1333(m), 1348(m), 1422(m), 1437(s), 1467(s), 1545(w), 1599(m), 1725(vs), 2848(vs), 2916(vs), 2950(s), 3044(w).

Preparation of polymers

Preparation of PMP. A three-necked flask was charged with nickel bromide (1.3 g, 6 mmol), triphenylphosphine (11.9 g, 46 mmol), zinc powder (12.1 g, 186 mg-atom) and DMF (60 ml). This reaction mixture was stirred at 45°C under an argon atmosphere. After 15 min, a red catalyst formed and HCMB (18.2 g, 60 mmol) in DMF (30 ml) was added. After the polymerization was conducted for 24 h, an excess of acetone was added to remove triphenylphosphine and unreacted monomer. The solid material was collected on a fritted filter, extracted with chloroform and reprecipitated in acetone.

PHMP was hydrolysed to produce PCMP by refluxing with 5% sodium hydroxide solution in propanol for 24 h. The reaction product was recovered and heated with hydrochloric acid in acetic acid at 90°C for 8 h. PCMP was decarboxylated by refluxing in quinoline in the presence of copper(II) oxide for 24 h to produce PMP. The reaction product was washed with acetone and then heated in hydrochloric acid to remove inorganic materials.

Synthesis of PDPP. MDCPB was polymerized in a similar way to MCPB. Solid material was recovered by pouring the polymerization mixture into acetic acid. It was dissolved in chloroform and reprecipitated in methanol containing hydrochloric acid. PMDPP was hydrolysed by refluxing with 10% sodium hydroxide solution in ethanol and PCDPP was recovered after adding hydrochloric acid. PCDPP was decarboxylated with copper(II) oxide in quinoline.

Measurements

T.g.a. The t.g.a. curves were recorded on a Rigaku TAS-200 thermal analyzer. The measurements were carried out from 100 to 800°C under nitrogen, using 3 mg of each sample. The heating rate was 20°C min^{-1}.

N.m.r. ^{1}H n.m.r. spectra were measured in deuterated chloroform on a JEOL GSX 270 spectrometer operating at 270 MHz at room temperature. Tetramethylsilane was used as internal standard.

I.r. spectra. I.r. spectra were measured using a KBr disc on a Perkin–Elmer 1720 FT-IR spectrometer.

Molecular weight determination. The molecular weight was measured in chloroform on a LC-908 gel permeation liquid chromatograph with JAIGEL-2H and -3H columns (Japan Analytical Industry Co. Ltd) at room temperature using polystyrene standard.

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