An attempt to synthesize regular cresolic resins through solid-state polycondensation

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p-Cresolic resins were synthesized by polycondensation of a monomer with 'dimeric' size (2,2'-dihydroxy-3-hydroxymethyl-5,5'-dimethyl-diphenylmethane, m.p. 136°C) in the solid state. A comparison was made with other products from polycondensation of the same monomer in the melt and in solution, and from reaction of *p*-cresol with formaldehyde. In the catalysed reactions, gaseous HCl or *p*-toluene sulphonic acid were used. Each raw product, after standard treatment in boiling toluene, gave a residue ('final product') which was always substantially insoluble, infusible and with noticeable X-ray crystallinity. Solid monomer polycondensation probably occurred in defect zones within the crystals. The crystallographic regularity of the final products appeared to decrease systematically by increasing the polycondensation temperature (from 90° to 175°C); critical changes in the transition from solid molten monomer polycondensation, possibly arising from topochemical effects, could not be clearly observed. The monomer crystal structure and the indexing of its powder X-ray diffraction spectrum were also determined.

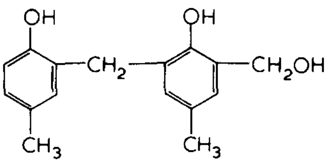
INTRODUCTION

Phenolic resins have a fairly complex chemistry. Several intermediate and final species can be formed in their synthesis with a variety of structures, and further chemical modifications can take place in subsequent (especially thermal) treatments[1]. It may be interesting to discover those synthesis conditions able to induce a higher degree of structual regularity of the products. Among these, solid state polycondensation of appropriate monomers can be considered.

In principle, cresolic monomers appear to be particularly suitable for forming regular molecular structures by polycondensation. In particular, *para*-substitution drastically reduces the number of possible constitutional irregularities expected when other phenolic monomers are used.

Here an attempt has been made to synthesize *p*-cresolic resins of improved structure regularity by polycondensation of an appropriate monomer in the solid state; comparisons with polycondensations in the melt or in solution were made. Reaction conditions have been selected in such a way that, on rational grounds, and from the previous phenolic resin literature, polycondensates with comparatively greater regular structure could be expected. The following choices were made:

(a) use of a single cresolic monomer, of a 'dimeric' size, of relatively high melting point (136°C), having the structure:



(H—2—CH$_2$OH)

(b) in catalysed reactions, use of acids as catalysts (gaseous HCl in bulk, and *p*-toluene sulphonic acid in solution);

(c) relatively low polycondensation temperatures.

For comparison, solution polycondensations were also performed using *p*-cresol and formaldehyde (introduced as trioxane), with a molar ratio *p*-cresol/formaldehyde greater than one.

The X-ray crystallinity of 'final products', defined as residues from the raw products after a standard inert solvent treatment (boiling toluene), has been assumed as a first criterion for estimating possible differences in structure regularity. It is of note that since molecular structure regularity is in general a necessary but not sufficient condition for the occurrence of crystallinity, this criterion, although frequently used with polymers, could be of questionable validity if applied without caution.

Structures such as phenolic resins should exhibit such conformational rigidity (or at least specific intra- and intermolecular interactions) that remarkable difficulties in crystallization are to be expected. Moreover, in cresolic resins high molecular weights cannot generally be reached (see for example, refs 1–4, 10). These are, at most, of the order of 1000–3000, but frequently even below 1000. Oligomer mixtures could thus appear as non-crystallizable products, even if single components were able to crystallize when isolated. Literature reports of the few cases in which X-ray observations have been made, indicate that these types of resins are largely amorphous[4–6], while single components have been observed to be crystalline, at least up to a tetrameric size[4]; in other cases, single components were treated as crystallizable, giving melting points, even up to the octamer[7–10].

In our work, crystallinity was observed in the polycondensation products after the chosen standard solvent treatment, which should result in a comparably crystallizing and fractionating effect on the products.

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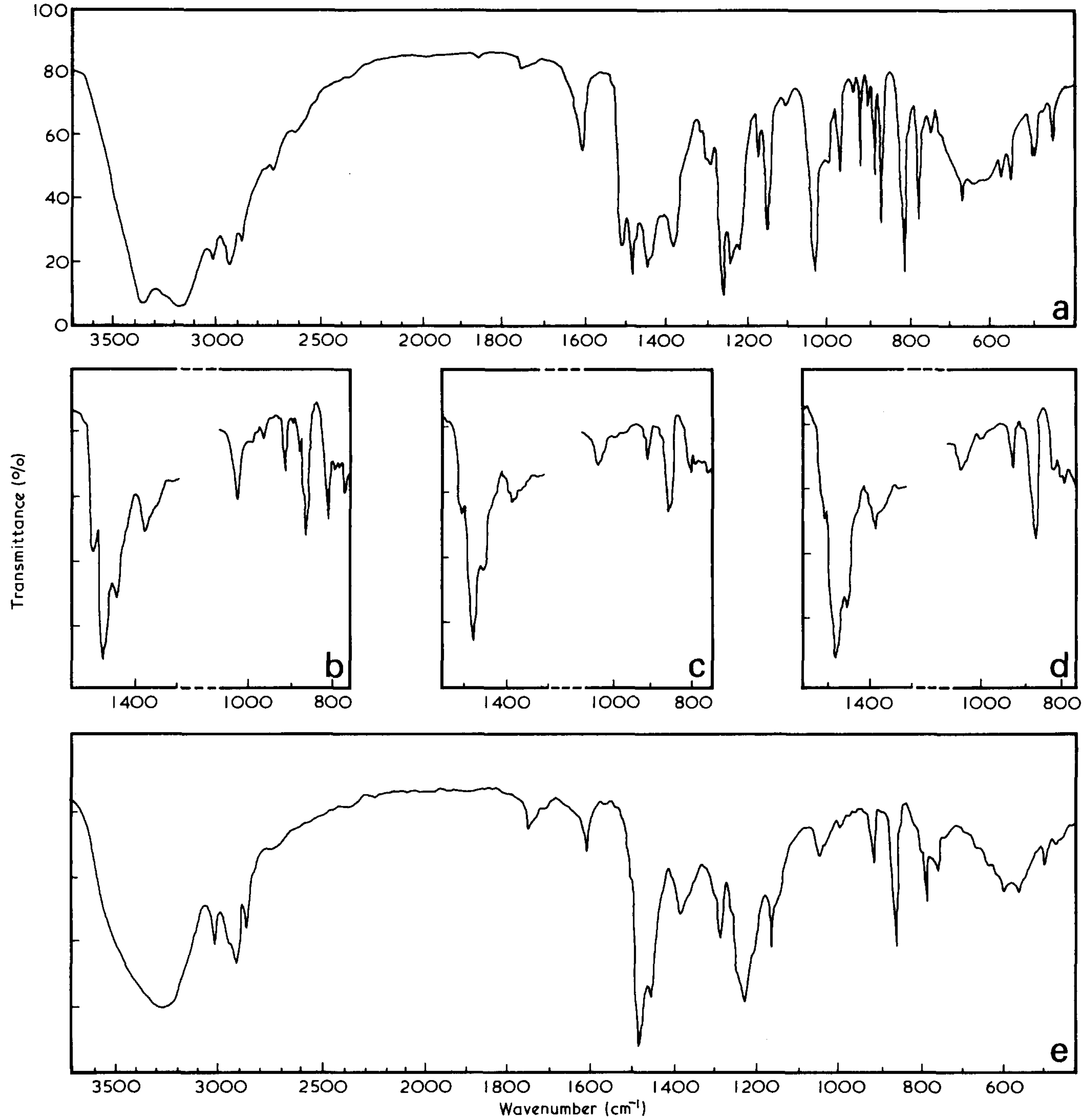


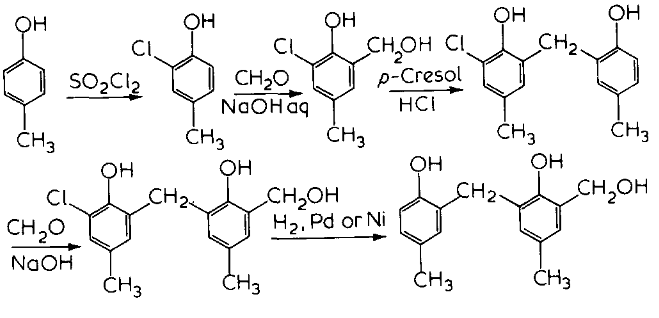
Figure 1 I.r. spectra of the reaction mixture at various stages of the solid monomer H—2—CH_2OH catalysed polycondensation at 90°C (run C2, *Table 2*): (a) monomer; (b) after 8 h; (c) after 16 h; (d) after 48 h; (e) final product (residue after boiling toluene treatment)

Hence, systematic differences observed in final product crystallinity should imply a significant difference in the structure regularity of corresponding synthesis products.

EXPERIMENTAL

Monomer synthesis and characterization

H-2-CH_2OH (2,2′-dihydroxy-3-hydroxymethyl-5,5′-dimethyl-diphenylmethane) was prepared according to Kämmerer[11], starting with 2-chloro-4-methylphenol. The synthetic path was as follows:



Brominated analogues were also used instead of chlorinated intermediates, but without substantial improve-

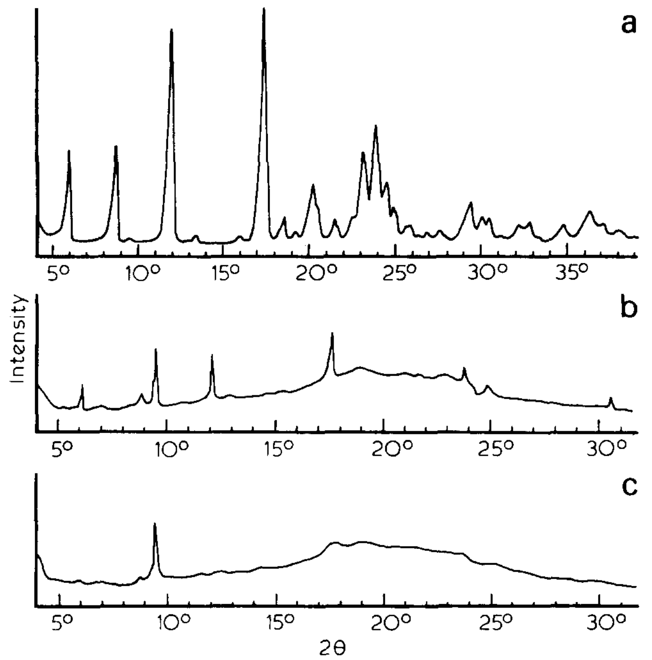


Figure 2 X-ray diffraction pattern of the reaction mixture at various stages of the solid monomer H—2—CH_2OH catalysed polycondensation at 90°C (run C2, *Table 2*): (a) monomer; (b) after 32 h; (c) after 48 h

ment in reactivities or in product yields. In all cases, intermediate and final products were characterized by infra-red (i.r.) and nuclear magnetic resonance (n.m.r.) spectroscopies, and elemental analysis.

The i.r. spectrum of H-2-CH_2OH, shown in *Figure 1a*, is in agreement with that previously reported by Grisenthwaite and Hunter[12]; the melting point, 136 C, is identical with that found by Adler[13] and Kämmerer[14].

The X-ray powder diffraction pattern of H-2-CH_2OH, crystallized from 1/1 vol/vol n-eptane/benzene solution, is reported in *Figure 2a*. The same pattern has been obtained by crystallization from benzene, ethanol and 4/1 vol/vol water/ethanol solution. In all cases considerable broadening of diffraction lines is observed, indicating small size or imperfection of crystallites.

Polycondensations

H-2-CH_2OH solid-state or melt polycondensations were carried out in a 100 ml cylindrical glass reactor, placed in a thermostatically-controlled oil bath. The powdered monomer sample (1–2 g) was placed on a porous tray, in an inner open container. A controlled dry HCl stream or a desired vacuum could be effected in the reactor.

Reference solution polycondensations were carried out in a round flask, in a thermostatically-controlled bath: a benzene/toluene mixture with b.p. 90 C was used as reaction solvent and *p*- toluenesulphonic acid added as catalyst.

Product separation and treatment

In the standard procedure, solid state or melt polycondensation mixture (1–2 g) was treated with boiling toluene (10–20 ml) for 2 h, and the residue taken to be as final product. In preliminary experiments other treatments and solvents (such as THF, acetic acid, chloroform, DMF, dioxane, tetraethylene glycol) were tested, and in some cases intermediate products were also considered and evaluated.

The polymer precipitated was only considered as raw product in the benzene/toluene solution polycondensations.

Wide-angle X-ray diffraction

Powder diffraction spectra were recorded with a Philips PW 1050 counter diffractometer, equipped with a graphite monochromator and pulse height analyser, using CuKα radiation. Measurements on single crystals were carried out with a Philips PW 1100 four-circle automatic diffractometer, using MoKα radiation.

Infra-red spectroscopy

I.r. spectra were recorded on a Perkin-Elmer 456 Spectrophotometer, using a few mg of solid samples in KBr pellets.

Differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.)

D.s.c. and t.g.a. were performed on a Mettler TA 2000 C apparatus at a heating rate of 8 C min^{-1} under a N_2 atmosphere.

Molecular weight

Measurements were made in chloroform at 35 C, using a Hitachi–Perkin–Elmer 115 vapour pressure apparatus.

RESULTS

Polycondensations

Table 1 reports the essential results of some polycondensations at 90°C under different conditions. Two runs using solid monomer H-2-CH_2OH are compared with two references in solution, where the monomer was in one case H-2-CH_2OH and in the other a mixture of *p*-cresol and formaldehyde (trioxane).

Table 1 Polycondensations at 90°C

Run	Monomer	Conditions	Products
A	*p*-Cresol/trioxane (mol. ratio: 3/1)	0.1144/0.0381 mol in 100 ml of benzene—toluene solution (5:3 vol); catalyst, *p*-toluene sulphonic acid (0.4 g); 48 h	Product precipitated in the reaction medium, 2.50 g; final product (residue from boiling toluene), 2.03 g
B	H—2—CH_2OH	0.0047 mol in 20 ml of benzene—toluene solution (5:3 vol); catalyst, *p*-toluene sulphonic acid (0.24 g); 48 h	Product precipitated in the reaction medium, 0.15 g; final product (residue from boiling toluene), 0.10 g
C2	H—2—CH_2OH	Solid monomer; catalyst: gaseous HCl (stream); 30 mmHg; 48 h	Weight of raw solid product, 1.24 g; final product (residue from boiling toluene), 0.50 g
D	H—2—CH_2OH	Solid monomer; catalyst, discontinuous treatment with gaseous HCl (see text); 0.1 mmHg; 18 h	No noticeable polycondensation

Table 2 Polycondensations of solid and molten H–2–CH_2OH monomer (m.p. 136°C)

Run	Temperature (°C)	Pressure (mmHg)	Catalytic conditions	Reaction time (h)	Final product*
C1	80	30	Gaseous HCl	18	No noticeable polycondensation
C2	90	30	" "	48	42%
C3	100	30	" "	8	34%
C4	110	30	" "	4	37%
C5	138	30	" "	3	54%
C6	170	30	No catalyst	4	39%
C7	175	0.1	" "	2.5	39%

* Wt % of the residue in the standard treatment with boiling toluene (with respect to raw reaction mixture)

In runs A, B, and C2 there was constant presence of catalyst, either as a dry HCl stream, or as dissolved *p*-toluene sulphonic acid. In the run D, gaseous HCl was introduced at the beginning in the reaction tube (in which there was solid H-2-CH_2OH under a vacuum of 0.1 mmHg) until atmospheric pressure was reached; after 10 min the HCl inlet was closed, the system pumped to a vacuum of 0.1 mmHg and maintained at that pressure for the duration of the reaction. After 4 h, HCl was again introduced until atmospheric pressure was reached and the operation cycle repeated. Under these conditions the system, did not reveal any noticeable extent of reaction.

Table 2 reports the essential results of polycondensations of solid or molten H-2-CH_2OH at different temperatures.

In run C1, at 80°C with HCl stream, no polycondensation was observed over 18 h, but polycondensation took place in a reasonable time above 80°C, with HCl stream at 90°–138°C on solid or molten monomer (m.p. 136°C), and without catalyst at 170°–175°C.

In run C4 it was observed that the powdered solid monomer at 110°C, showed some collapse immediately after the injection of HCl.

In some cases the course of the polycondensation was followed by recording the i.r. spectra of samples withdrawn at different times. The spectra recorded during run C2 (*Figures 1b–1d*) provide an example of reaction development. In particular, the reaction may be monitored by the gradual attenuation of the three bands at 805, 875 and 1510 cm^{-1}, and of the band at 1030 cm^{-1}, respectively assignable to the 1,2,4-trisubstituted benzene ring and to the hydroxymethyl group[12,15–17].

X-ray diffraction spectra have also been recorded during some solid monomer polycondensations. An example may be seen in *Figure 2*, relating to run C2. Along with the intensity decrease of the reflections characteristic of solid H-2-CH_2OH, the simultaneous formation of a broad band of an amorphous raw product is observed. It is interesting to note that besides an intensity decrease, the monomer peaks undergo a gradual sharpening, and that different intensity changes take place for different crystallographic directions.

Figure 3 reports the thermocalorimetric and thermogravimetric behaviour of H-2-CH_2OH. Clearly, the sharp endothermic melting peak is immediately followed by an exothermic deviation up to ~200°C; this is associated with a weight loss of about 7%, attributable to spontaneous polycondensation. The system seems then relatively stable until 340°C, where exothermic processes (probably degradative) take place.

Products

The final products (residues from boiling toluene) of all the polycondensations exhibited evident X-ray crystallinity. They proved to be largely insoluble in a variety of solvents and in the thermal analysis reached pyrolysis temperatures without noticeable deviations from the baseline. Their i.r. spectra, an example of which is given in *Figure 1e*, follow a common pattern without noticeable differences among them, and exhibit strong similarities to those recorded by Kämmerer and Niemann[17] for cresolic compounds of the type CH_3-*n*-CH_2OH, with $n \geq 4$ (n is the number of aromatic rings bound by methylene bridges).

The residues from boiling toluene were in general highly insoluble in THF, chloroform, dioxane, DMF, tetraethylene glycol and in other common organic solvents. This high insolubility drastically reduced the possibilities of further characterization, in particular molecular weight determination.

In order to obtain at least a rough indication of the molecular weight of the polycondensation products, a reference polycondensation of H-2-CH_2OH has been performed in dioxane solution, with *p*-toluene sulphonic acid, at 90°C, whose product precipitated in water, could be completely dissolved in chloroform. Its number-average molecular weight was of the order of 1800. By subsequent treatment with acetic acid and toluene, products similar to those reported in *Figures 5c* and *5d* were obtained.

The X-ray diffraction profiles of all the final products show, as a common feature, the occurrence of more or less broad diffraction peaks at 2θ values of about 5.0°, 9.5°, 18.0°, 20.0° and 23.0°, corresponding to repeat distances of 17.7, 9.3, 4.9, 4.4 and 3.9 Å. However, systematic differences among diffraction patterns are also apparent. The largest number of crystalline reflections is found for the product of the solution polycondensation of H-2-CH_2OH at 90°C (run B), followed by the products of *p*-cresol/trioxane polycondensation at 90°C (run A) and of a solid-state H-2-CH_2OH polycondensation at the same temperature (run C2). By increasing the polycondensation temperature, the intensity distribution of the diffraction profiles becomes gradually more continuous, so that only the cited repetition distances are clearly recognizable.

No definite trend with temperature was observed for the variation in the relative amounts of final products with respect to raw materials (*Table 2*).

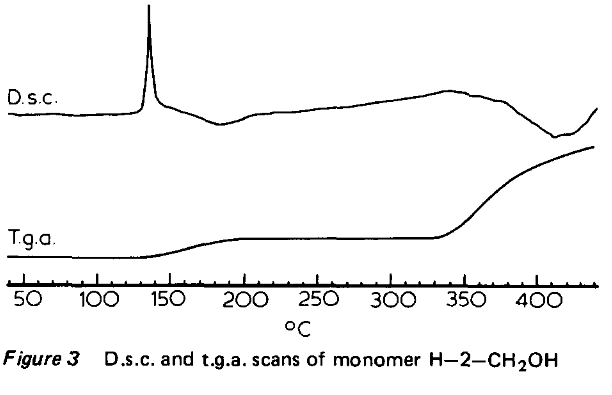


Figure 3 D.s.c. and t.g.a. scans of monomer H–2–CH_2OH

Table 3 Indexing of powder diffraction pattern of H–2–CH_2OH

$h\,k\,l$	d_c* (Å)	d_0 (Å)	I/I_0
1 0 0	14.620	14.73	40
0 1 0	10.088	10.07	44
$\bar{1}$ 1 0	9.138	9.21	5
2 0 0	7.310	7.36	89
$\bar{2}$ 1 0	6.526	6.53	6
2 1 0	5.456	5.47	6
$\bar{1}$ 2 0	5.068	5.08	100
$\bar{3}$ 1 0	4.749	4.77	15
$\bar{2}$ 2 0	4.569	4.57	8
0 0 1	4.396	4.38	27
1 0 1 3 1 0	4.180 4.099	4.13	11
$\bar{2}$ 1 1	3.931	3.917	15
2 2 0	3.831	3.837	39
$\bar{1}$ 2 1 2 0 1	3.726 3.725	3.723	50
$\bar{4}$ 1 0 4 0 0	3.662 3.665	3.648	29
2 1 1 $\bar{2}$ 2 1	3.580 3.531	3.562	18
1 2 1 $\bar{3}$ 1 1	3.456 3.435	3.453	11
3 0 1 3 2 0	3.223 3.218	3.220	8
$\bar{3}$ $\bar{1}$ 1 $\bar{3}$ 3 0 0 $\bar{2}$ 1	3.051 3.046 3.030	3.040	19

* Calculated from single crystal data

Preliminary experiments have been undertaken into the solubility and crystallinity of intermediate products. After the polycondensation of solid H-2-CH_2OH at 100°C, the raw reaction mixture was found to be amorphous from the X-ray spectrum of *Figure 5a*. This raw product was substantially (not completely) soluble in boiling tetrahydrofuran (THF). By pouring the cold solution in n-heptane, 1.06 g of raw product gave 0.83 g of a precipitate with noticeable crystallinity, (spectrum, *Figure 5b*); the soluble portion, recovered by solvent evaporation, was amorphous. The precipitate in cold acetic acid reduced to a residue of 0.77 g, (spectrum, *Figure 5c*), with only slightly higher crystallinity. The latter product in boiling toluene gave a residue of 0.30 g, (spectrum, *Figure 5d*), with markedly improved crystallinity. If the raw product or the n-heptane precipitate were treated directly with boiling toluene, a greater amount of final product was obtained, with crystallinity quite similar to that obtained by the treatment above.

Monomer crystal structure

The X-ray diffraction data obtained in this investigation have made possible the determination of the crystal structure of H-2-CH_2OH.

Single crystals were grown from a 4:1 water/ethanol solution. From X-ray diffraction data obtained on a four-circle diffractometer, unit cell dimensions were determined and refined by a least-squares method (estimated standard deviations in parentheses): $a = 14.913(1)$ Å; $b = 10.494(1)$ Å; $c = 4.4943(5)$ Å; $\alpha = 79.09(1)°$; $\beta = 93.73(1)$; $\gamma = 101.28(1)°$. Space group, $P1$ or $P\bar{1}$; $Z = 2$ molecules per unit cell; $D_x = 1.270$ g cm^{-3}.

The powder diffraction pattern could be indexed on the basis of the single crystal data, as shown in *Table 3*. It is of note that indexing beyond 2θ values of 30° becomes rather meaningless, because of low crystal symmetry and broadening of diffraction lines.

DISCUSSION

From *Tables 1* and *2* it may be seen that polycondensation of solid H-2-CH_2OH does not take place (at least in reasonable reaction times) without the continuous presence of catalyst, or below a temperature of 90°C (see run C1 at 80°C). When catalysed, the reaction is possible in a temperature range some tens of degrees below the monomer melting point (136°C). This, combined with the way in which the monomer X-ray diffraction peaks disappear during the reaction (*Figure 2*), suggest that solid monomer polycondensation occurs only in defect zones of the crystalline monomer. Results do not allow us to

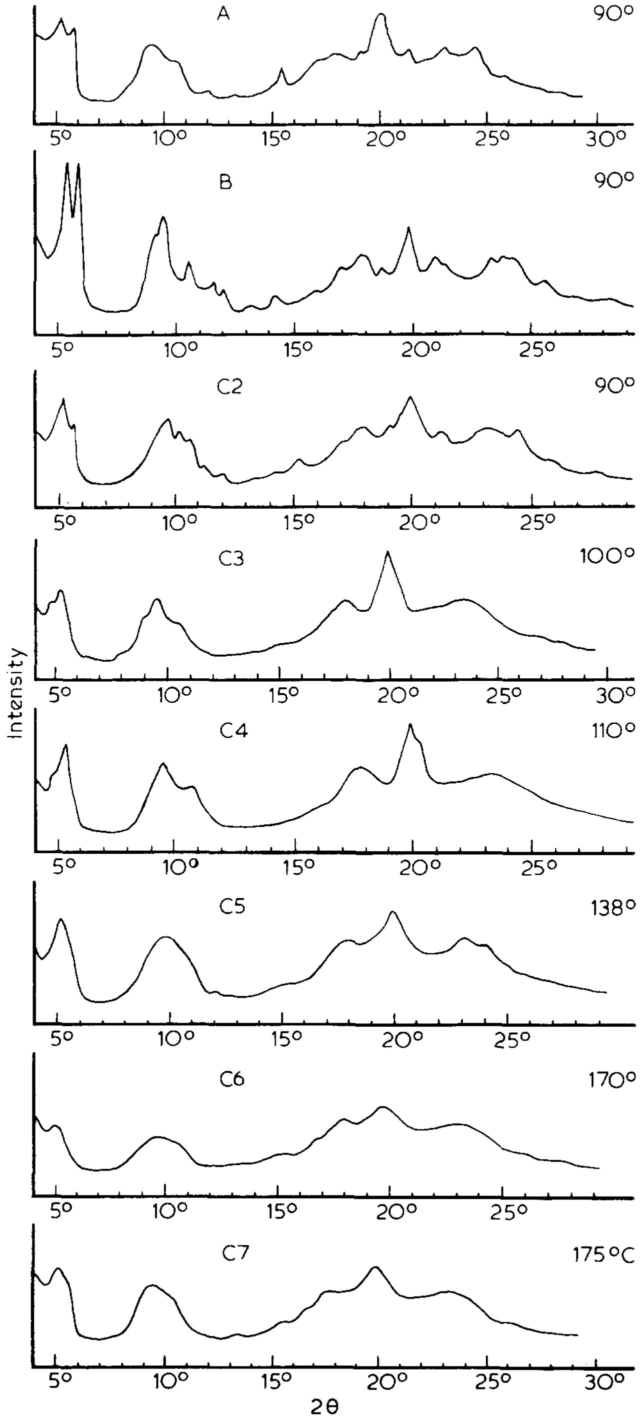


Figure 4 X-ray diffraction pattern of the final products of bulk and solution polycondensations of *Tables 1* and *2*

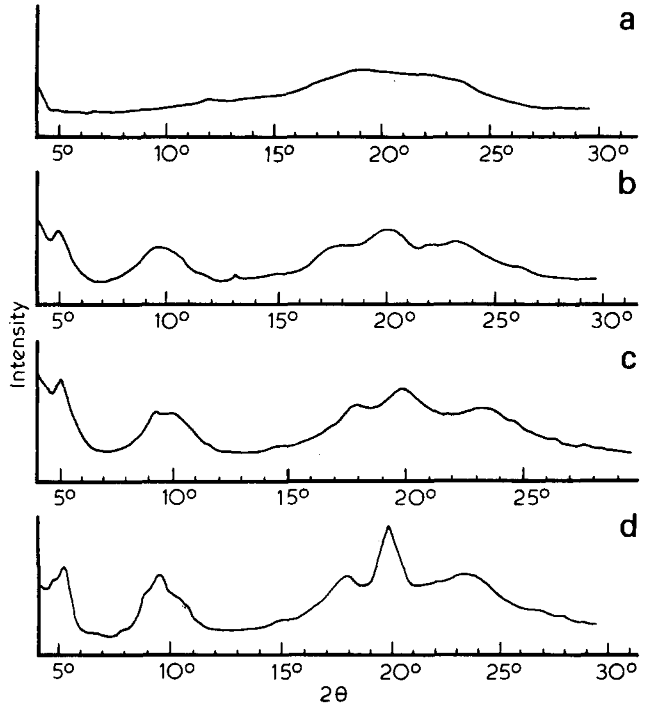


Table 5 X-ray diffraction pattern of raw reaction mixture, intermediate and final product by different solvent treatments (run C3, 100°C, *Table 2*); (a) reaction mixture; (b) precipitate from the THF/reaction mixture solution poured in n-heptane; (c) residue to cold acetic acid extraction of the precipitate under (b); (d) residue to a subsequent treatment with boiling toluene

deduce whether some topochemical effect is present under these circumstances: the raw products are in any case amorphous, and no critical changes can be noticed in the final product regularity when passing (by raising the temperature) from solid to melted monomer polycondensation (*Figure 4*).

The final products (obtained as residues of the raw products by standard boiling toluene treatment) exhibit in all cases a noticeable crystallinity, which appears to be systematically affected by synthesis temperature: it is comparatively good when the reaction temperature is low (90°–100°C), and gradually poorer as the reaction temperature is increased.

Infusibility and insolubility of the final products are properties not supported by previous literature observations on low oligomeric phenolic and cresolic resins. These are invariably described as compounds with definite, moderately high melting points, soluble in common polar and non-polar organic solvents (including toluene). For low molecular weight components, infusibility and insolubility might resemble the behaviour observed by Hayes and Hunter[8] of the cyclic *p*-cresolic tetramer, where by specific thermal treatment, the tetramer is transformed into a hypothetical hemihydrate. However, it may be noted that the various polycondensation conditions, and the toluene treatment used in our investigation are in general far from the conditions reported[8] as favouring the formation of both the cyclic tetramer and of its hypothetical hemihydrated form.

The final products of our investigation cannot be regarded as consisting prevalently of a single, easily-crystallizable low oligomeric species mixed with higher non-crystallizable entities, as suggested by Hunter and Vand X-ray observations[4], according to which it seems that only species up to the tetrameric one should be crystalline. The X-ray spectra of our final products (*Figures 4* and *5*) are not typical of a mixture of well-crystallized and amorphous substances, but rather of materials with a low degree of crystallographic regularity.

A more probable conclusion is that our final products are the highest molecular weight fractions of the raw products, namely mixtures of homologous, high oligomeric terms, with substantial molecular structure regularity, that mutually interfere in a collective crystallization process, possibly with different crystallizing abilities. If so, two hypotheses can be set forth. By raising the synthesis temperature, the molecular regularity of the final products could be gradually reduced, so that a lowering of the degree of crystallographic regularity is actually observed. Alternatively, or at the same time, the polycondensation could reach gradually higher extents of reaction by increasing the reaction temperature; this would lead to raw products with some gradually higher average molecular weight, and consequently to final products with lower crystallizing ability. The latter hypothesis, however, might seem in contrast with already cited literature, which suggest that *p*-cresolic resins cannot increase their average molecular weights beyond a few thousands.

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