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Crystallizable cresolic resins by homosaligenin polycondensation

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(*Received* 24 *December* 1981)

Acid catalysed polycondensations of homosaligenin (H–1–CH_2OH) were carried out with monomer in the solid state at 50°C, in the melt at 138°C and in a benzene/toluene or dioxane solution at 90°C. Crystallizable products were obtained, possibly after a boiling toluene treatment. The yields and X-ray crystallinity of the products from the melt and benzene/toluene solution reactions, compare well with those previously obtained with the corresponding monomer of dimeric size (H–2–CH_2OH).

Keywords Cresolic resins; polycondensation; homosaligenin; crystallinity; thermogravimetry

INTRODUCTION

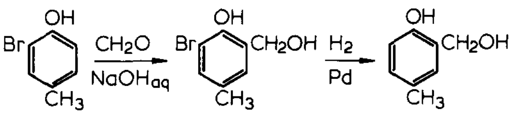
In a preceding paper[1] it was shown that by thermal or HCl catalysed polycondensation of solid and molten 2,2′-dihydroxy-3-hydroxymethyl-5,5′-dimethyldiphenylmethane (briefly: H–2–CH_2OH; m.p. 136°C), at temperatures from 90° to 175°C, a crystalline product could be obtained in substantial yields (from 37% to 54%) as the residual fraction of the amorphous raw products treated with boiling toluene.

Apparently the same crystalline product could be obtained by polycondensation of the same monomer, as well as of *p*-cresol and formaldehyde, in a benzene/toluene solvent mixture, at 90°C, with *p*-toluene sulphonic acid as catalyst. The final crystalline product could not be completely characterized, in that it was infusible up to decomposition (ca. 320°C) and practically insoluble in a variety of organic solvents. All the experimental observations suggested that it probably was a higher molecular weight portion of the overall product.

Some exploratory work is described in this report, in order to understand whether comparable results could also be obtained by corresponding polycondensations of homosaligenin (1-hydroxy-2-hydroxymethyl-4-methylbenzene; H–1–CH_2OH; m.p. 106°C), used instead of the above monomer of 'dimeric' size (H–2–CH_2OH), in the solid state, in the melt and in benzene/toluene or dioxane solution.

EXPERIMENTAL

Homosaligenin was synthesized according to Kämmerer[2], starting with 1-hydroxy-2-bromo-4-methylbenzene:



Intermediate and final products were characterized by infra-red spectroscopy, X-ray diffractometry and elemental analysis. Purity of H–1–CH_2OH, a white crystalline powder whose melting point (106°C) is in good agreement with that reported by Kämmerer[3] and Megson[4], was checked by thin layer chromatography, using silica gel as the adsorbent and an ethanol/chloroform (1/9 vol/vol) mixture as eluent.

Polycondensations of solid or molten H–1–CH_2OH were carried out in a 100 ml cylindrical glass reactor, and solution polycondensations in a round-bottomed flask, both placed in a thermostatically controlled oil bath, as described in ref. 1.

The raw polycondensation products (1–2 g) were subsequently treated with boiling toluene (10–20 ml) for 2 h and the residue was taken as 'final product'.

0032–3861/82/060928–04$03.00

Wide angle X-ray powder diffraction spectra were recorded with a Philips PW 1050 counter diffractometer or with a Philips PW 1024 Debye–Scherrer camera, using CuKα radiation. I.r. spectra were obtained with a Perkin–Elmer 456 Spectrophotometer, using a few milligram samples in KBr pellets. Differential scanning calorimetry (d.s.c.), thermogravimetric analysis (t.g.a.) and derivative thermogravimetry (d.t.g.) were performed on a Mettler 2000 C apparatus, at a heating rate of 10°C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

The monomer was first tested in its behaviour towards heating. In *Figure 1*, the d.s.c. thermogram shows a sharp fusion peak, A, around 106°C, followed by a diffuse endothermic lowering, B, then a broad exotherm, C, up to ~230°C; after this a steadiness zone, D, takes place until decomposition, E, beyond ~350°C.

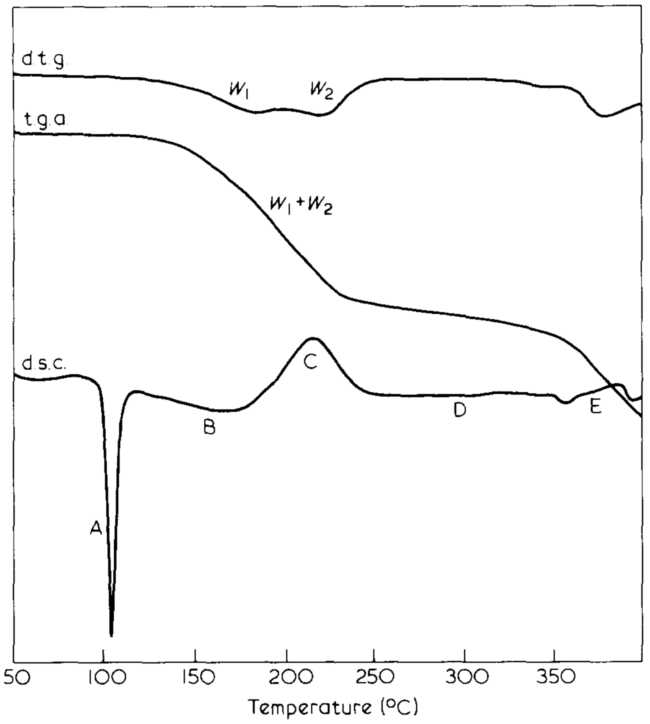


Figure 1 D.s.c., t.g.a. and d.t.g. scans of monomer H–1–CH_2OH

From the t.g.a. thermogram, in the B+C interval a marked weight loss W_1+W_2 (about 25% of the initial weight) is observed; in the same interval the d.t.g. curve reveals, with two bands, that this loss is due to at least two successive phenomena, by which two nearly equal weights W_1 and W_2 are lost. This behaviour may be interpreted as the release of about one molecule of water, per one molecule of monomer, in a thermal polycondensation, probably preceded by the freeing of another water molecule retained in the monomer by absorption or crystallization.

Table 1 shows the results of some acid-catalysed polycondensations of H–1–CH_2OH in dioxane or benzene/toluene solution at 90°C, as well as those with solid and molten monomer at 50° and 138°C respectively. The final product yields (residue in the standard boiling toluene treatment) are indicated, and compared, when possible, with the yield values previously obtained[1] in corresponding polycondensations of H–2–CH_2OH. It can be seen that they are substantially similar, for the two monomers, in the runs in benzene/toluene (M2) and with molten monomer (M4), while they differ in the case of the solid monomer (M3).

The X-ray diffraction patterns of the final products of runs M2, M3 and M4 are reported in *Figure 2* and compared respectively with those from corresponding H–2–CH_2OH polycondensations (runs B, C2 and C5 of ref. 1): one can again observe that the patterns of the final products of runs M2-B and M4-C5 are quite similar, while a comparatively lower crystallinity appears in the final product of run M3 with respect to that of run C2.

For the polycondensation of the two solid monomers, one cannot easily find conditions for a more direct comparison, because the polycondensation of solid H–2–CH_2OH has proved[1] to be difficult or very slow below 90°C, and H–1–CH_2OH at this temperature is already

Table 1 Results of polycondensations

Run	Reaction conditions	Temperature (°C)	Reaction time (h)	Yield of final product* (crystalline) from H–1–CH_2OH (this work)	from H–2–CH_2OH (ref. 1)
M1	0.43 mol l^{-1} of monomer in the solvent (dioxane) Catalyst: *p*-toluene sulphonic acid, 0.04 mol l^{-1}	90	48	6.0%*** (0.5%)	(not determined)
M2	0.43 mol l^{-1} of monomer in the solvent (5 : 3 vol benzene-toluene mixture) Catalyst: *p*-toluene sulphonic acid, 0.04 mol l^{-1}	90	48	9.0% (18.4%)**	8.2% (run B, 90°C) (12.3%)**
M3	Solid monomer Catalyst: gaseous HCl (stream) Pressure: 5 mm Hg	50	40	15.8%	39.1% (run C2, 90°C) 31.6% (run C3, 100°C) 34.4% (run C4, 110°C)
M4	Molten monomer Catalyst: gaseous HCl (stream) Pressure: 5 mm Hg	138	3	37.6%	50.2% (run C5, 138°C) 36.3% (run C6, 170°C) 36.3% (run C7, 175°C)

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

** Crystalline product precipitated in the reaction medium, taken as raw product for comparison with ref. 1

*** The soluble part in the reaction medium, precipitated in water, was taken as raw product (in parentheses: the crystalline product precipitated during reaction)

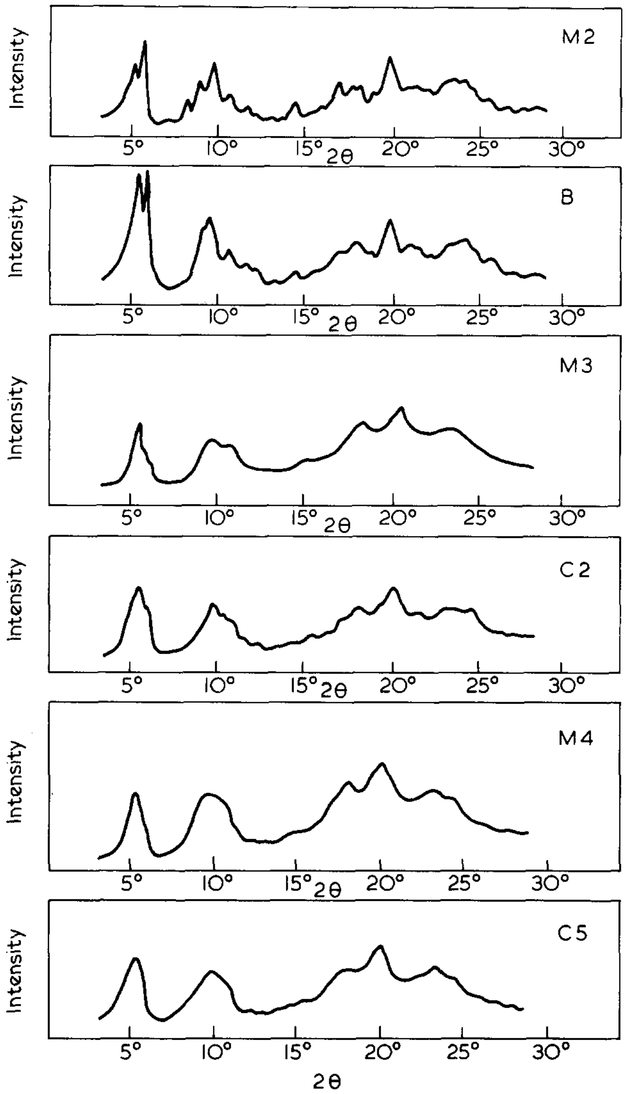


Figure 2 Wide angle X-ray diffraction patterns of final products of solution and bulk polycondensations of *Table 1*

near its melting point of 106°C. We observed in run M3 at 50°C (as well as in other exploratory runs at 60°–80°C) that the crystalline powder of H–1–CH_2OH underwent a type of quasi-liquid collapse at the beginning of the reaction, and became, in a relatively short time, a mass with a glassy appearance. Also i.r. spectra confirmed that the reaction had practically stopped after short time. This behaviour may be understood as a consequence of the fact that local reaction heat and release of water make the monomer molecules particularly mobile and reactive, but after a relatively short time the monomer transforms into low oligomers with much higher melting point and with lower mobility. These oligomers are physically similar to solid H–2–CH_2OH and are therefore much less reactive at that temperature.

The results from run M1 in dioxane, a better solvent compared with toluene or benzene/toluene mixtures, require special comment. The crystalline product precipitated during the reaction was almost negligible, and the final product was obtained in a relatively small amount (see *Table 1*). I.r. spectra indicated that the reaction extent in dioxane was lower than in the benzene/toluene mixture for a given time and temperature, and therefore the average molecular weight of the overall product ought to have been lower.

Figure 3 compares the Debye–Scherrer photographs of three different samples: M1.a (a), the boiling toluene residue of the raw product which stayed in dioxane solution throughout the reaction (recovered by precipitation in water); M1.b (b), the small portion of crystalline product precipitated during the same reaction in dioxane; M2.f (c), for comparison, the final product of run M2 (reaction in benzene/toluene mixture).

From solubility considerations and qualitative analysis of i.r. spectra, M1.a had an average molecular weight lower than M1.b (and M1.b lower than that of M2.f). Indeed the X-ray pattern of M1.a shows numerous sharp diffraction lines more typical of low molecular weight compounds. Conversely sample M1.b follows a pattern quite similar to that of normal final products, like M2.f, even though for M2.f the boiling toluene treatment probably led to a slightly improved crystallinity (treatment and effected with M1.b, because of its very small amount).

CONCLUSIONS

The acid catalysed polycondensation of solid homosaligenin (H–1–CH_2OH) did not take place, for kinetic and physical factors, in a way corresponding to that previously observed with the solid 'dimeric' monomer H–2–CH_2OH[1]. In fact, conditions could not be found to keep the system in a solid state throughout the reaction and to secure a high degree of reaction, although a product with a portion crystallizable from boiling toluene was obtained as in previous work.

However, results corresponding to previous work with H–2–CH_2OH, were obtained by homosaligenin polycondensation in the melt and in benzene/toluene solution, with final products of similar X-ray crystallinity and comparable yields.

Polycondensation of homosaligenin in dioxane allows comparison of X-ray patterns of crystalline products with different average molecular weights.

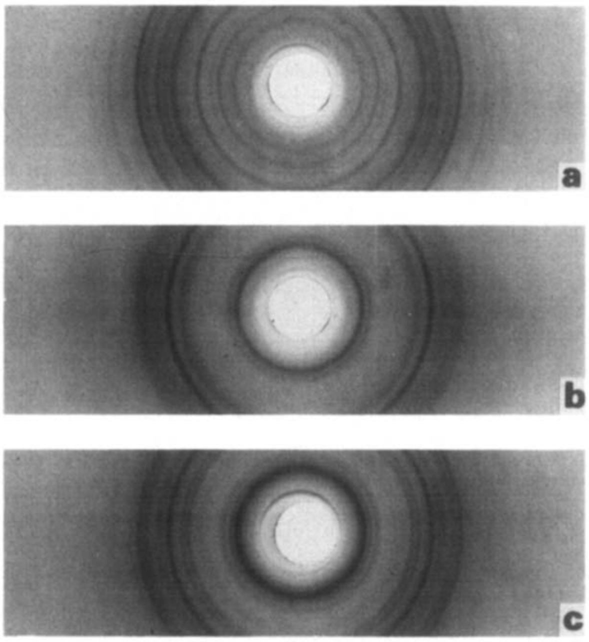


Figure 3 Debye–Scherrer photographs of two portions of the product of run M1 in dioxane ((a) M1.a; (b) M1.b and, for reference, of the final product of run M2 ((c) M2.f) (see text)

ACKNOWLEDGEMENTS

This work was undertaken with financial support from Consiglio Nazionale delle Ricerche (CNR), and Ministero della Pubblica Istruzione, Rome. The authors are indebted to Dr Paolo Cardillo of the Stazione Sperimentale per i Combustibili, S. Donato, Milan, for his assistance with the calorimetric and thermogravimetric measurements.

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Study by scanning electron microscope of phosphorylated polyethylene resins

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(*Received* 13 *October* 1981)

A study of surface area using specific resins for uranium from phosphorylated polyethylene has been made. A positive correlation between maximum capacities of the resins and surface area was found. The crosslinked resins with polyols present the best maximum capacities and high adsorption capacities. This is in agreement with the electron micrographs which give information about the adsorption process.

Keywords Polymer matrix; ion-exchanger; phosphonate resins; crosslinked; maximum capacities; adsorption

INTRODUCTION

Phosphorylated organic compounds, by virtue of the electron donating phosphoryl oxygen, have the strongest complexing properties for salts such as uranyl nitrate and lithium chloride.

In order to facilitate manipulation and the subsequent recovery of the complexing phosphoryl ligands it is desirable that they be incorporated into an insoluble polymer matrix with the hope that they would still retain their complexing properties and selectivity, while having physical properties similar to conventional ion-exchangers[1]. Judging from the behaviour of monomeric phosphoryl compounds[2] it is likely that non-ionic polymers of the phosphine type would have sufficiently enhanced complexing strengths to permit high adsorption of metallic salts from aqueous systems.

Resins of the sample phosphonate type ($R-PO(OH)_2$, $R = $ resin) are clearly more selective for the uranyl ion than for resins containing aminophosphonate or aminocarboxylate functional units. Resins having monoacetic functional units of the former type such as the polymerized allyl phosphonate, are much more selective than those containing diacidic functional units such as the polystyrene methylene phosphonates and they later show a high affinity for alkaline earths which makes elution more difficult[3].

The phosphorylated polyethylene resins, crosslinked with diamines and diols, effectively retain uranium as UO_2^{2+}. Thus, they show a higher capacity and selectivity towards Fe(III) and Re(VII)[4] than the commercially used Amberlite IRA-400.

Here we report on surface area and morphological studies by scanning electron microscopy. Phosphorylated polyethylene (PE-4) was crosslinked with ethylenediamine (PE-9), ethyleneglycol (PE-17), diethyleneglycol (PE-18) and triethyleneglycol (PE-17), respectively.

EXPERIMENTAL

Determination of maximum capacities

A 250 ml beaker containing dry resin (1.0 g) and uranyl acetate pentahydrated aqueous solution (100 ml) (equivalent to 4 g of uranium per litre) was placed in a thermostatically controlled bath at 25°C. The mixture was agitated for 2 h at 200 cycles per minute. The aqueous solution was separated by decanting and washed several times with water. This process was repeated twice using the same resin, and using a uranium solution (100 ml) of the same initial concentration. Uranium was analysed by spectrophotometry[5] and the uranium fixed in the resin is determined from the difference.

Determination of surface area

The surface areas of the different resins were determined by the adsorption of a solute from liquid phase method, using an aqueous solution of ammonium chloride at 20°C a transverse section in the ammonium chloride molecule of 31 (Å)^2 was considered[6]. The amount of nitrogen was determined by using the Kjeldahl method[7].

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