polymer reports

Photo-energy transfer in polystyrene–polyphenylene oxide blends

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Examination of the fluorescence intensities and lifetimes of xylenol, poly(2,6-dimethyl phenylene oxide) and polystyrene shows that energy transfer between these components is very efficient both in dilute solution and in solid blends. Quenching of excited polystyrene by poly(2,6-dimethyl phenylene oxide) is accompanied by stabilization against photo-oxidative degradation.

INTRODUCTION

Photo-oxidation of polystyrene-poly(2,6-dimethyl phenylene oxide) (PS–PPO) blends has been shown to depend on oxygen diffusion and the onset of localized molecular motion in the solid[1,2]. However, the blend has greater stability than PS despite the greater ease of low amplitude localized motion (β-process) in PPO. Consequently, it is of interest to examine the photo-physical primary processes which precede the chemical steps of photo-oxidation.

Photo-degradation processes require the energy, initially contained in an incident photon, to be absorbed by some chromophore, and then transferred to the site of chemical activity. In very dilute solutions this migration is mainly intra-chain, although a small number of inter-chain transfers are possible. In solid polymers both inter- and intra-macromolecular transfers may occur. Intra-chain migration of singlet energy in PS is well documented[3–5] but there is, at present, no evidence for a similar phenomenon in PPO, or of interchain transfer between these two species. Since the orientation of nearest neighbour aromatic chromophores in PPO is not that required for efficient energy transfer (or excimer formation) it is not obvious whether excitation energy is very localized, or can wander over a large interaction distance, in such a polymer.

The objectives of this work were to characterize the important absorbing chromophores in PS–PPO blends, to use measurements of fluorescence intensities and lifetimes as indicators of the efficiency of energy transfer between the two macromolecules, and to ascertain whether any correlation exists between energy transfer and photochemical stabilization.

EXPERIMENTAL

Materials

Commercial polymers were purified by multiple precipitation from tetrahydrofuran, and dried in a vacuum oven. Xylenol (B.D.H.) was purified by multiple recrystallization from benzene.

Solvent, tetrahydrofuran, was fractionally distilled over $LiAlH_4$.

Techniques

Steady state spectra were obtained on Perkin Elmer 402 and MPF-44 spectrometers. Fluorescence lifetimes were measured on a high resolution nanosecond spectrometer based on the design of Birch and Imhof[6]. Photodegradation was carried out using a low pressure mercury lamp with emission maximum at 254 nm and with an irradiation intensity of $1.6 \times 10^{-8} E$ cm^{-2} s^{-1}. Molecular weights were measured using the single point viscosity method[7], and converted to quantum yields for main chain scission in the normal way[8–10].

RESULTS AND DISCUSSION

The absorption and fluorescence emission spectra of polystyrene (PS), poly(2,6-dimethyl phenylene oxide) (PPO) and xylenol (X) (the monomer from which PPO is synthesized) are illustrated in *Figure 1*. PPO and xylenol have molar decadic extinction coefficients at λ_{max} of 2.5×10^3 and 1.7×10^2 respectively. The spectra of commercial PPO show strong absorption and emission due to residual xylenol monomer and xylenol-like chain ends.
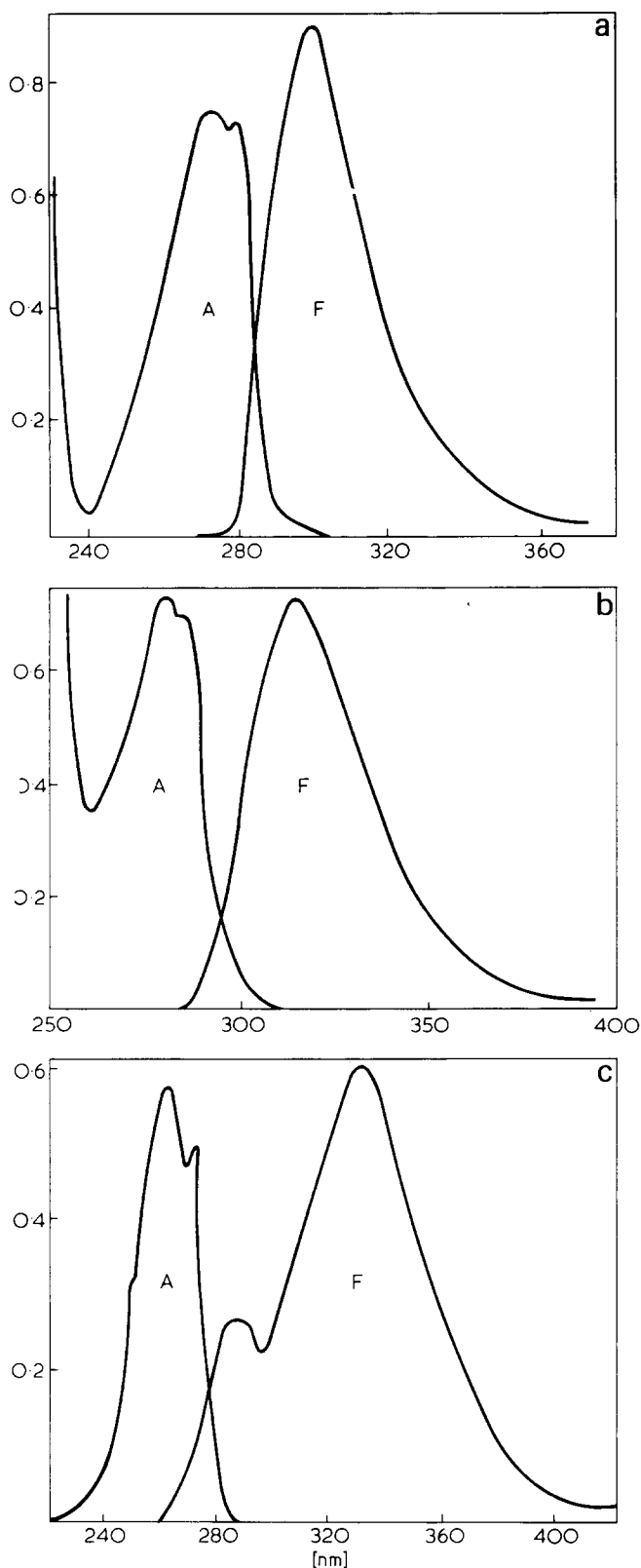
Figure 1 Absorption (*A*) and fluorescence emission (*F*) spectra of dilute solutions in tetrahydrofuran of (a) 2,6-xylenol, (b) poly(2,6-dimethyl *p*-phenylene oxide), (c) polystyrene. Amplitudes are in arbitrary units

energy transfer to either PS or PPO. In dilute solution both PS and PPO quench xylenol fluorescence, *Figure 2*. Stern–Volmer plots of the intensity data have slopes of 78 l m^{-1} and 1176 l m^{-1} (where concentrations are monomer residues in polymer) for PS and PPO respectively. The measured fluorescence lifetime of xylenol in tetrahydrofuran is 4.9 ns[11], so that the bimolecular rate constants are 1.6×10^{10} l m^{-1} s^{-1} and
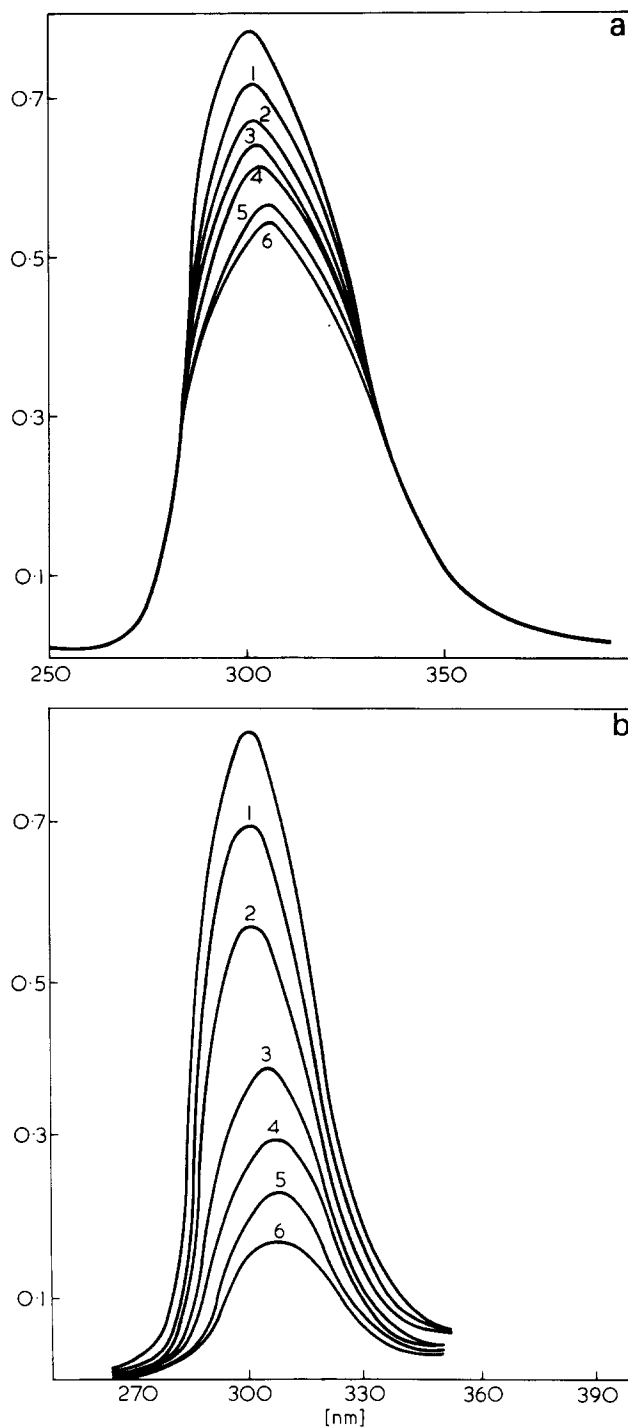

Figure 2 Fluorescence of xylenol (1 x 10^{-3} m l^{-1} in tetrahydrofuran at 25°C) quenched by (a) polystyrene: 1, 1.3 x 10^{-3} m l^{-1}; 2, 2.1 x 10^{-3} m l^{-1}; 3, 3.1 x 10^{-3} m l^{-1}; 4, 3.9 x 10^{-3} m l^{-1}; 5, 4.4 x 10^{-3} m l^{-1}; 6, 5.2 x 10^{-3} m l^{-1}, and (b) poly(2,6-dimethyl *p*-phenylene oxide): 1, 2.0 x 10^{-4} m l^{-1}; 2, 2.5 x 10^{-4} m l^{-1}, 3, 3.8 x 10^{-4} m l^{-1}; 4, 5.0 x 10^{-4} m l^{-1}; 5, 6.3 x 10^{-4} m l^{-1}; 6, 7.4 x 10^{-4} m l^{-1}. Amplitudes are in arbitrary units and concentrations are of monomer residues

The role of xylenol monomer

Since xylenol is an absorbing species one mechanism of photochemical excitation could involve primary light absorption by xylenol (at high xylenol levels) followed by

2.4×10^{11} 1 m^{-1} s^{-1} respectively. As an indicator of energy transfer efficiency we use the approximate Smoluchowski equation

$$k_q = \frac{4\pi r_{AB} D_{AB}}{10^3}$$

where r_{AB} is the energy capture radius and $D_{AB} = D_A + D_B$ is the diffusion coefficient for relative movement of energy donor and acceptor. Setting $D_{polymer} \ll D_x \simeq 1 \times 10^{-9}$ m^2 s^{-1} the energy transfer radii are 2 nm and 32 nm respectively. There are a number of reasons why these numbers are semi-quantitative only, the most important being the use of a statistical concentration of monomer segments when these are constrained into local high and low concentrations by the distribution of macro-chains. Nevertheless, the large transfer radii so calculated do suggest that monomer residues distant from the excited species can receive the energy rather more efficiently than would be expected by way of a single Förster resonance step. The overlap integral for PPO–X is greater than for PS–X, so that transfer to this latter species is more efficient. Thus monomer impurity could be a photosensitizer of oxidative degradation in commercial blends.

Energy transfer from polystyrene

Solid PS is stabilized by blending with PPO, despite the greater ease of β-molecular motion in the latter polymer. One reason for this could be transfer of photoenergy from PS to PPO. The fluorescent emission from PS exhibits both monomer and excimer bands, the former showing overlap with PPO absorption, and the latter being swamped by PPO emission. Thus transfer of energy from PS to PPO can be seen in the diminution of PS monomer emission, and the replacement of PS excimer emission (peak at 330 nm) by PPO emission (peak at 315 nm). The energy transfer in dilute solution (2.95×10^{-3} mol 1^{-1} monomer residue in THF) and in solid films is illustrated in *Figure 3*. Because overlap of the PPO emission makes estimates of energy transfer from intensity data unreliable, lifetime data have been used for this purpose, *Table 1*. Expression of the decay curve as two exponentials

$$F(t) = A_{1 exp}(-t/\tau_1) + A_{2 exp}(-t/\tau_2)$$

shows that the relatively wide band pass of the nanosecond spectrometer admits emission from both PS excimer and PPO, and that the relative intensity of the short-lived PPO component increases with even minute quantities of this quencher. The decrease in the lifetime of PS can be subjected to Stern–Volmer analysis, when the slope is 5.2×10^3 1 mol^{-1} (of PPO monomer residue). Assuming a mutual diffusion coefficient of 2×10^{-11} m^2 s^{-1}, the interaction distance is estimated as order of magnitude 10^3 nm. Despite the semi-quantitative nature of the analysis, quenching efficiencies of this magnitude are possible only if the donor energy is effectively available over the whole of the PS macro-coil, and all the monomer segments of the PPO chain are able to quench the excited PS.

In the solid films the emission from PS at 330 nm is markedly non-exponential, and the two lifetimes recorded here, *Table 2*, both contain contributions from the true excimer lifetime.
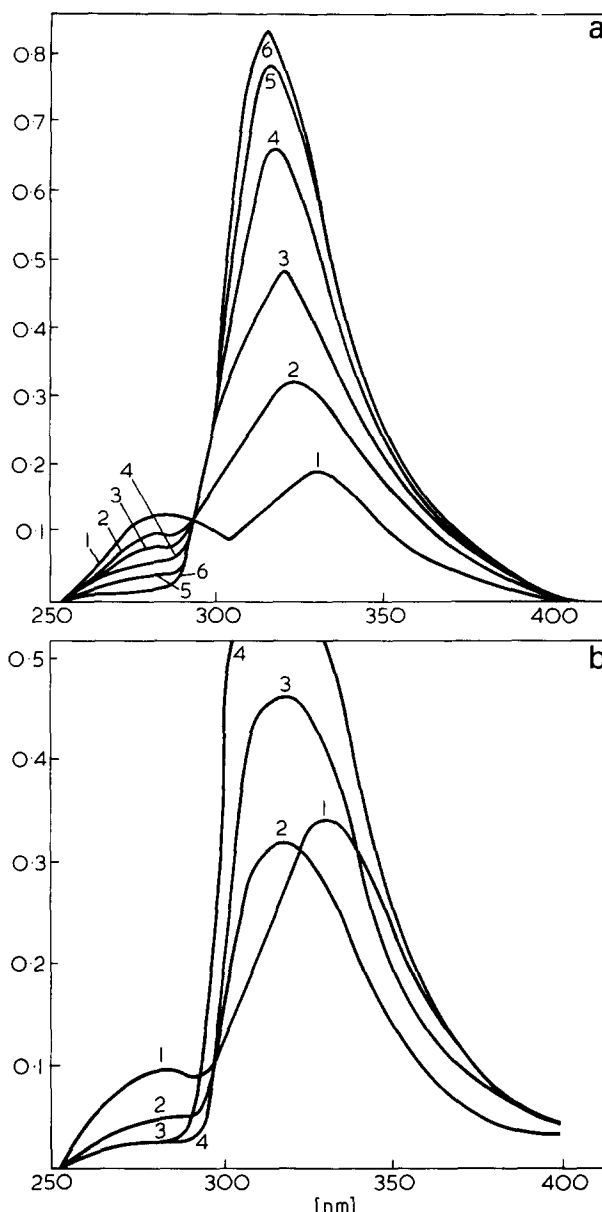

Figure 3 Fluoresence of polystyrene quenched by poly(2,6-dimethyl p-phenylene oxide) at 25°C. (a) 2.7×10^{-3} m l^{-1} styrene residues in tetrahydrofuran: 1, PPO zero; 2, 0.43×10^{-4} m l^{-1}; 3, 0.83×10^{-4} m l^{-1}; 4, 4.3×10^{-4} m l^{-1}; 5, 1.74×10^{-4} m l^{-1}; 6, 2.61×10^{-4} m l^{-1}; (b) in solid films: 1, no PPO; 2, 2 wt % PPO; 3, 4 wt % PPO; 4, 15 wt % PPO

Table 1 Lifetime of PS (2.9×10^{-3} mol l^{-1} monomer residue) quenched by PPO in THF at 25°C. $\lambda_{excitation}$ 265 nm, $\lambda_{emission}$ 330 nm

10^4 PPO concentration (mol l^{-1} monomer)	τ_1 (ns)	A_1	τ_2 (ns)	A_2	χ^2
0	12	1.0	—	—	0.9
0.24	11.3	0.71	1.1	0.01	1.3
1.3	8.4	0.58	1.2	0.05	1.5
2.0	6.4	0.68	1.1	0.06	1.6
3.8	4.9	0.65	1.1	0.08	1.2
12 (no PS)	—	0	0.9	1.0	0.9

The complexity of the photophysical processes is such that the double exponential analysis does no more than illustrate the decreasing lifetime and amplitude of PS emission (decreasing τ_1, A_1 up to 15 wt% PPO) and

increasing amplitude of short-lived PPO emission (A_2). Nevertheless, the data clearly show that energy transfer from PS to PPO is efficient in the solid blend, and at 15 wt% almost all the emission is from PPO $(A_2/A_1 \gg 1)$. Without knowledge of the molecular compatability of PS–PPO, i.e. the radial distribution of PPO segments around excited PS, it is not possible to enumerate the transfer probability.

Photodegradation of PS–PPO solutions

Solutions of PS $(9.6 \times 10^{-2}\,\text{mol}\,1^{-1})$ monomer units in tetrahydrofuran were irradiated at 254 nm in the presence of various quantities of xylenol, xylenol dimer, methylated xylenol dimer and PPO. The viscosities of the various solutions were monitored as a function of time, and the number of main chain scissions calculated after 150 min irradiation, *Figures 4* and *5*. The very efficient stabilization by PPO is immediately apparent.

Values of Φ (quantum yield in the presence of quencher)/Φ_0 (PS alone) were plotted against the concentration of quencher in the conventional Stern–Volmer fashion, and the slopes are reported in *Table 3*.

The magnitude of the stabilization by PPO represented by the slope is smaller than the energy transfer characteristics observed in the lifetime measurements, indicating that chain scission arises from energy more

Figure 5 Number of chain scissions per macromolecule, S, for various PS–PPO blends (9.6×10^{-4} m 1^{-1} PS monomer segments) in tetrahydrofuran at 298K

Table 2 Lifetime of PS–PPO films at 25°C. $\lambda_{\text{excitation}}$ 265 nm, $\lambda_{\text{emission}}$ 330 nm

Wt. % PPO	τ_1	A_2	τ_2	A_2	χ^2
0	14.4	0.26	25.5	0.29	1.5
4	16.9	0.05	1.1	0.01	1.7
15	13.4	0.005	0.99	0.6	2.1
100	2.7	0.05	0.4	0.7	1.7

Table 3 'Stern–Volmer' slopes for molecular weight decrease of PS in presence of xylenol and PPO solutions in THF at 30°C

Quencher	Stern–Volmer slope (1 mol^{-1} of monomer residue)
Xylenol	870
Xylenol dimer	850
PPO	85
Methylated xylenol dimer	80

localized than the mobile excitons observed in the quenching of 'monomer' fluorescence. Also comparison of the hydroxy and methoxy dimeric compounds illustrates that a proton transfer reaction is a necessary part of the degradation step.

Thus it appears that photo-excitation energy transfer from PS to PPO and to xylenol are effective stabilization processes (at low concentrations of the latter). *Figure 5* closely resembles a plot of fluorescence intensity at 319 nm against blend composition published very recently by Jensen and Kops[12]. These authors conclude that the decrease in PS excimer fluorescence is greater than can be explained by absorption of PPO at the excitation wavelength. The extinction coefficients and very high transfer efficiencies reported in this paper support a resonance transfer mechanism (as opposed to collisional quenching or simple screening). Of course, the fact that excimer emission is reduced and that energy capture occurs over large distances are not incompatible since it is the very mobile monomer exciton which is quenched (*Figure 3*), and thus the flow of energy into trapping excimer states is interrupted.
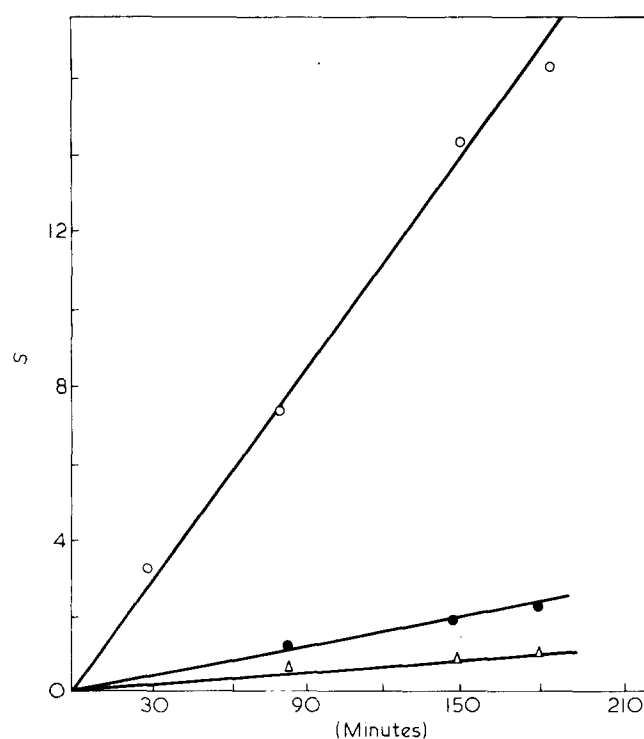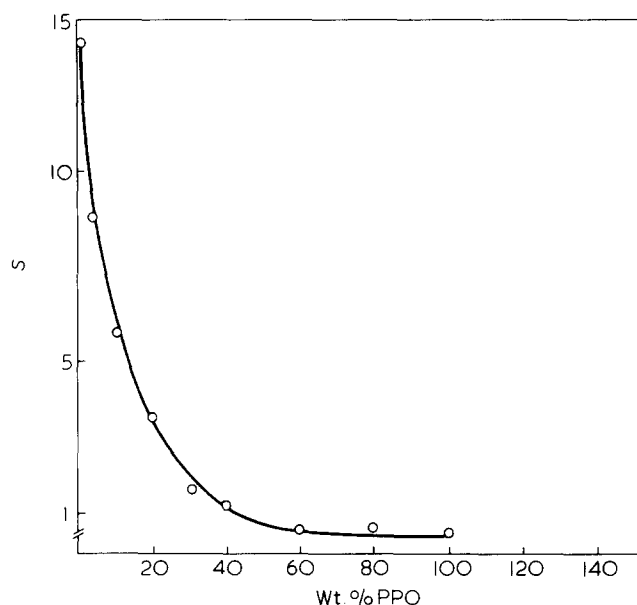

Figure 4 Number of chain scissions per macromolecule, S, for polymer 1 × 10^{-3} m 1^{-1} in tetrahydrofuran at 298K. ○, PS; ●, 70 wt % PS and 30 wt % PPO; △, PPO

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Crystallizable cresolic resins by homosaligenin polycondensation

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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' - dimethyldiphenyl - methane (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:
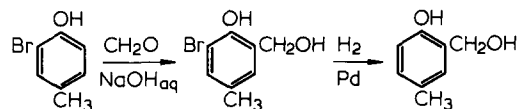
Intermediate and final products were characterized by infra-red spectroscopy, X-ray diffractometry and elemental analysis. Purity of $H-1-CH_2OH$, a white crystalline powder whose melting point (106°C) is in good agreement with that reported by Kämmerer[3] and Megson[4], was checked by thin layer chromatography, 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'.