

Poly(*ortho*-vinylbenzophenone)

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This article reports the synthesis and free radical polymerization of *ortho*-vinylbenzophenone. The glass transition temperature T_g of the homopolymer is 136°C. The products synthesized appeared to be atactic and amorphous. The Mark-Houwink constants for poly(*o*-vinylbenzophenone) in tetrahydrofuran are $K = 4.2 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$ and $a = 0.765$. The pre-exponential constant under theta conditions, K_θ , is estimated to be $5.93 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$. The ratio of unperturbed dimensions of the actual polymer and free rotating analogue chain is 3.93, which is almost double that of polystyrene. The Flory-Huggins interaction parameter for poly(*o*-vinylbenzophenone)/tetrahydrofuran is 0.48 at room temperature. The $k_p/k_t^{1/2}$ ratio at 60°C is $1.1 \times 10^{-2} \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$. In free radical copolymerizations with styrene at 70°C, r_1 (*o*-vinylbenzophenone) = 1.216, $r_2 = 0.751$. This copolymerization is virtually random.

Keywords Poly(*ortho*-vinylbenzophenone); *ortho*-vinylbenzophenone; styrene; copolymer; kinetics; polymerization

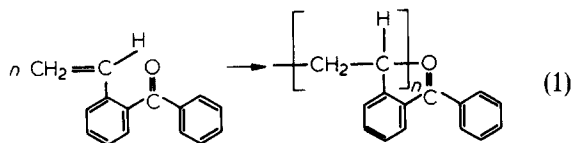
INTRODUCTION

Here we report on the synthesis and free radical polymerization of a new monomer, *ortho*-vinylbenzophenone. Some physical and solution properties of the polymer are described and reactivity ratios for radical copolymerization of this monomer with styrene are also given.

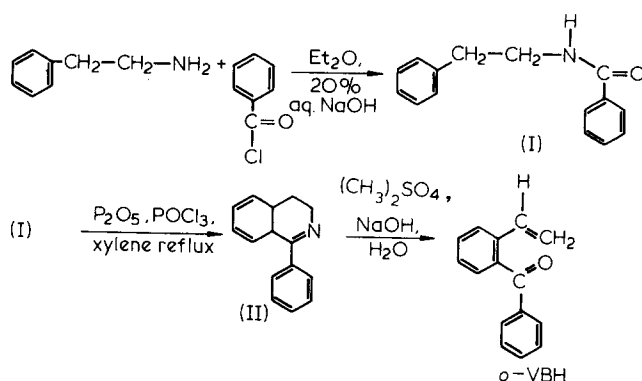
RESULTS

The *o*-vinylbenzophenone (*o*-VBP) monomer was prepared by the reactions shown in Scheme 1. Cyclization of the benzamide (I) to 1-phenyl-3,4-dihydroisoquinoline (II) was accomplished using a modification of the technique described by Whaley and Hartung¹, and gave higher yields (>95%) than other reported methods². The conversion to *o*-vinylbenzophenone was accomplished using the method of Gensler and coworkers³. Significant monomer losses due to polymerization were noted when the temperature of the reaction mixture was allowed to exceed 90°C. Otherwise, yields in excess of 85% were obtained.

Free radical homopolymerizations were carried out in bulk monomer and in solution. In both cases *o*-VBP polymerized readily despite the steric bulk of the pendant benzophenone moiety:



The polymer is a white solid which may be cast into films from tetrahydrofuran and toluene. It is readily soluble in these solvents and in benzene and chlorinated hydrocarbons, but appears to be insoluble in ether, acetone and lower alcohols. This behaviour resembles that of polystyrene, as would be expected.



The infra-red spectra of the monomer and polymer are shown in *Figure 1*. The spectrum of the monomer shows a strong carbonyl absorption at 1665 cm^{-1} and a weak C=C stretching band at 1630 cm^{-1} . The disappearance of the C=C absorption at 1630 cm^{-1} and the subsequent appearance of paraffinic C-H stretching bands at $2850\text{--}2950 \text{ cm}^{-1}$ indicate that the polymerization occurred at the vinylic site as shown in reaction (1). The ultra-violet spectra of the monomer and polymer are similar to that of benzophenone, having $\pi\text{--}\pi^*$ and $n\text{--}\pi^*$ transitions at approximately 252 and 344 nm, respectively. The salient features of the ultra-violet spectra are listed in *Table 1*.

The proton n.m.r. spectrum of *o*-vinylbenzophenone monomer (60 MHz, CDCl_3 solution) shows an aromatic multiplet at $7.2\text{--}7.9 \delta$ and a typical ABX pattern ($H_a \sim 5.14 \delta$, $H_b \sim 5.65 \delta$ and $H_x \sim 6.8 \delta$) attributed to the vinylic protons. Integration is consistent with the proposed structure.

The ^{13}C n.m.r. spectrum of the polymer (20.1 MHz, CDCl_3 solution) is shown in *Figure 2*. The carbonyl peak appears at 197.0 ppm and there are aromatic peaks in the 125–145 ppm range and methylene and methine signals at 42 and 36 ppm, respectively. Peak assignments were made by comparison with values calculated from the additivity rules summarized by Wehrli and Wirthlin⁴. All the peaks,

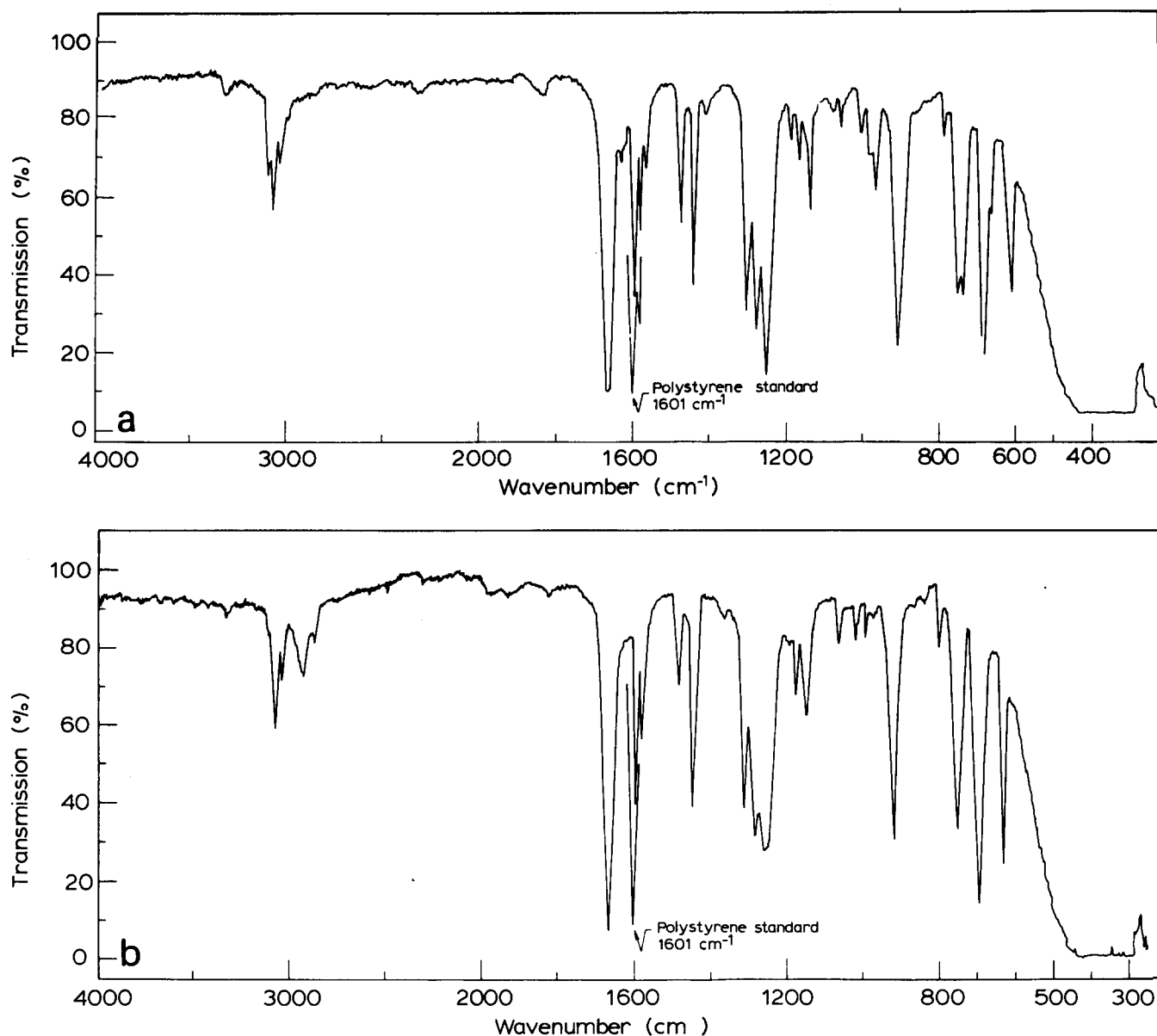


Figure 1 (a) Infra-red spectrum of *o*-vinylbenzophenone. (b) Infra-red spectrum of poly(*o*-vinylbenzophenone) film cast from tetrahydrofuran solution

Table 1 Ultra-violet absorption characteristics of *o*-VBP, poly(*o*-VBP) and benzophenone in tetrahydrofuran

Transition		<i>o</i> -VBP	Poly(<i>o</i> -VBP)	Benzophenone)
$\pi \rightarrow \pi^*$	λ_{max} (nm)	251	252	252
	ϵ_{max} (l mol ⁻¹ cm ⁻¹)	14 900	19 000	15 800
$n \rightarrow \pi^*$	λ_{max} (nm)	344	342	344
	ϵ_{max} (l mol ⁻¹ cm ⁻¹)	135	162	128

except for carbonyl, were broad, with the methylene and methine especially so (peak width at half height ~ 50 to 100 Hz). This is broader than the peaks in the spectrum of polystyrene in a solution with about the same viscosity in CDCl₃. None of the poly(*o*-VBP) peaks exhibited fine structure (both at 20.1 MHz and at 80 MHz) which could

be related to tacticity of the polymer. The polymer is assumed to be atactic since the method of synthesis is not likely to yield a stereoregular product, although the ¹³C spectrum provides no information on this point.

Glass transition temperatures measured by differential scanning calorimetry (d.s.c.) averaged 136°C with considerable scatter which obscured any molecular weight effects which may have been present. The *T_g* values of a series of low molecular weight *o*-VBP/styrene copolymers were also measured to provide a reliable value for the glass temperature of poly(*o*-VBP). (These copolymers were all made by bulk copolymerization at 70°C, using 8.4 mg azobis(isobutyronitrile) initiator per gram of monomers.) The relevant data are listed in Table 2. These results were fitted to the equation⁵:

$$\frac{1}{T_g} = \frac{w_A}{T_{gA}} + \frac{w_B}{T_{gB}} \quad (2)$$

where *T_g* is the glass temperature of a copolymer which contains weight fraction *w_A* of monomer A (here styrene)

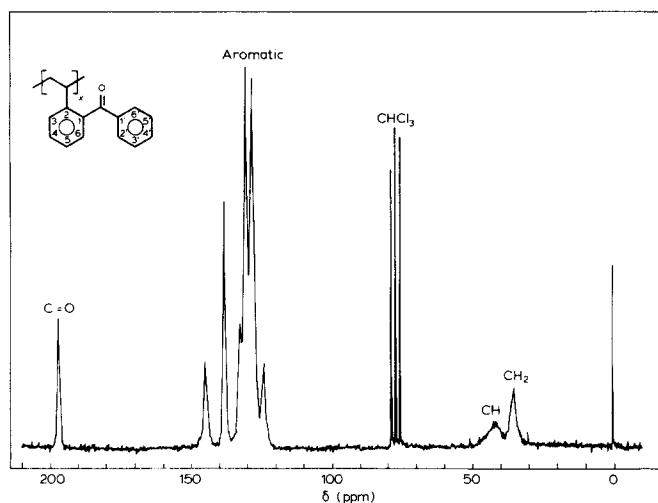
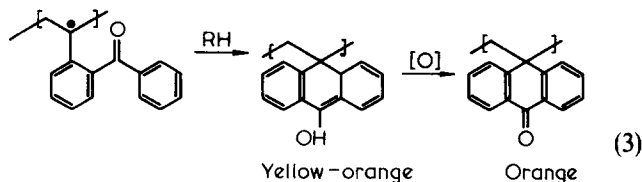


Figure 2 ^{13}C n.m.r. spectrum of poly(*o*-VBP) in CDCl_3 solution at 20.1 MHz

Carbon	δ (ppm, TMS)
Carbonyl	197
2	145.0
1 and 1'	138.1
4 and 4'	132.5
6, 2', 6'	130.5
3, 3', 5'	128.3
5	124.0
methylene	42
methine	36

and weight fraction w_B of *o*-VBP. In this case T_{gA} is 358K (Table 2) because of the low molecular weight of the polystyrene sample and T_{gB} (poly(*o*-VBP)) is to be determined. A plot of $1/T_g w_B$ versus $w_A/T_{gA} w_B$ should have a slope of unity and intercept equal to $1/T_{gB}$. The data actually fit a linear least-squares plot with slope 0.9953 and an R^2 value of almost 1. The intercept produces a T_g value for poly(*o*-VBP) of 408.5K, in good agreement with the values measured on homopolymers. As expected, the greater bulk of the substituent in poly(*o*-VBP) results in a higher T_g than that of polystyrene, which is at 373K.

No crystal melting point was observed by either d.s.c. or d.t.a. Visual inspection of poly(*o*-VBP) samples in the heating block of the d.t.a. apparatus indicated that the polymer samples studied here started to flow at about 180°C. The polymers yellowed substantially on further heating beyond this temperature and the yellow-orange melt underwent rapid decomposition at temperatures near 345°C. Analogy to the Elbs reaction⁶ suggests that an anthraquinone-like thermolysis product may be responsible for the strong colouration of the melt:



The colouration could also be due to semiquinone/quinone radicals.

Copolymers with styrene appeared to be thermally

stable under the conditions in which the homopolymers discoloured and decomposed.

The constants K and a for poly(*o*-VBP) in the Mark-Houwink equation:

$$[\eta] = K\bar{M}^a \quad (4)$$

were determined using the gel permeation chromatography-intrinsic viscosity method described elsewhere^{7,8}. This technique requires two broad molecular weight distribution polymers with different intrinsic viscosities. Samples with intrinsic viscosities of 8.80 and $64.65 \text{ cm}^3 \text{ g}^{-1}$ were used to estimate values of $K = 4.20 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$ and $a = 0.765$, in tetrahydrofuran solution. These Mark-Houwink constants were used to calibrate the gel permeation chromatograms of the poly(*o*-VBP) polymers which were made.

The rate of vinyl polymerizations by free radical initiation can be expressed by the familiar formula:

$$R_p = \frac{k_p(fk_d[I]_0 e^{-k_d t})^{1/2} [M]}{k_t^{1/2}} \quad (5)$$

where R_p is the instantaneous rate of polymerization, $[M]$ is the monomer concentration, $[I]_0$ is the initial concentration of initiator, f and k_d are the initiator efficiency and dissociation rate constant, t is time and k_p and k_t are the rate constants for propagation and termination, respectively. Extension of this formula allows for estimation of conversion (equation (6)) and kinetic chain length, ν (equation (7)), and hence number average molecular weight:

$$-\ln \frac{[M]}{[M]_0} = \frac{2k_p(f[I]_0)^{1/2}}{k_t^{1/2} k_d} [1 - \exp(-\frac{1}{2}k_d t)] \quad (6)$$

$$\nu = k_p[M]/2(fk_d k_t [I])^{1/2} \quad (7)$$

Monomer concentration, as measured by the gas-liquid chromatography method described in the Experimental section, is plotted as a function of reaction time in Figure 3. R_p is taken as the slope of this plot. By substituting 60°C values for k_d ($1.2 \times 10^{-5} \text{ s}^{-1}$)⁹ and f (0.6)¹⁰ for azobis(isobutyronitrile) initiator into equation (5), the $k_p/k_t^{1/2}$ ratio can be calculated at various reaction times. The results, which are summarized in Figure 4, show that this ratio was essentially constant at low conversions, but increased rapidly once the polymerization had progressed beyond 50% conversion of mo-

Table 2 Glass transition temperatures of *o*-VBP/styrene copolymers (samples characterized by mole percentages of *o*-VBP in copolymer)

<i>o</i> -VBP (mol %)	T_g (K)*
0	358.4
0.6	360.1
1.3	362.9
3.6	363.1
5.5	364.8
11.3	367.8
33.3	372.8
66.8	381.1

* T_g extrapolated to $1^\circ \text{C min}^{-1}$ d.s.c. heating rate

nomer. This behaviour is attributable to a drop in the value of k_t as the reaction proceeds and is probably a manifestation of the 'gel effect' resulting from reduced diffusion rates of macroradicals at concentrations and molecular weights where entanglements are possible. The propagation rate constant, k_p , is not significantly affected under these conditions since the monomer is still reasonably mobile.

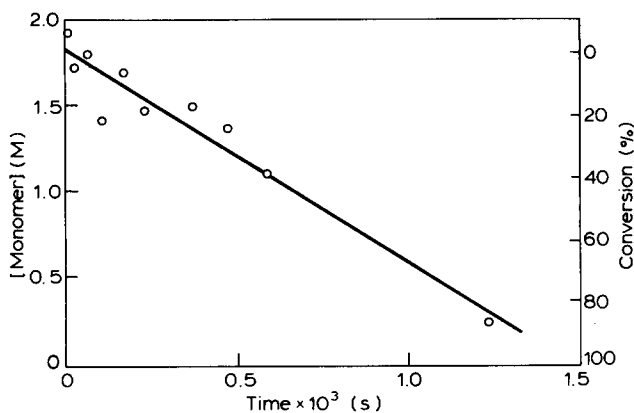


Figure 3 Monomer concentration vs. time for *o*-VBP polymerization in toluene solution at $60^\circ \pm 0.5^\circ\text{C}$. Initial AIBN concentration = 0.1504 M. Each point is an average of at least two gas chromatographic measurements

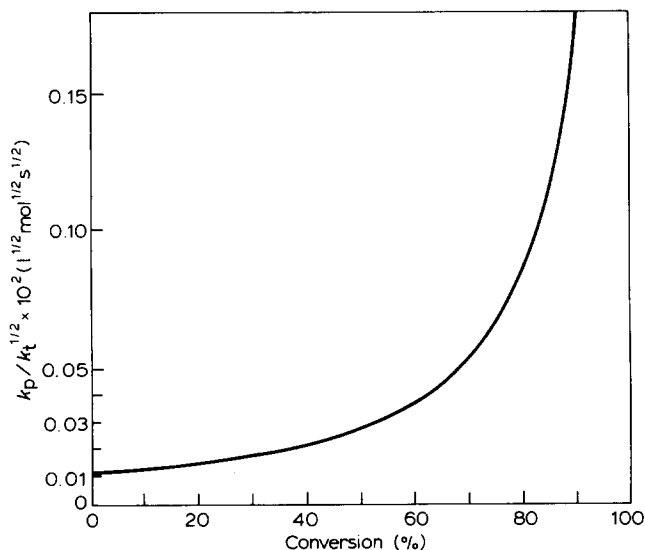


Figure 4 Ratio of $k_p/k_t^{1/2}$ as a function of conversion. The values plotted are from the data of Figure 3

The low conversion value of $k_p/k_t^{1/2}$ is $1.1 \times 10^{-2} \text{l}^{1/2} \text{mol}^{-1/2} \text{s}^{-1/2}$. An estimate of this ratio was needed to plan the polymerization experiments in the first place and data for *o*-methylstyrene were used since both this monomer and *o*-VBP are substituted in the same position on the phenyl ring. With the reported k_p of $60 \text{ litre mol}^{-1} \text{s}^{-1}$ for *o*-methylstyrene¹¹ and k_t for styrene¹² of $3.6 \times 10^7 \text{ litre mol}^{-1} \text{s}^{-1}$, the $k_p/k_t^{1/2}$ ratio for *o*-VBP was guessed to be about $1 \times 10^{-2} \text{ litre}^{1/2} \text{mol}^{-1/2} \text{s}^{-1/2}$, which is close to the value found experimentally.

Individual values for the rate constants k_p and k_t require measurements using rotating sector¹³ or spatially intermittent polymerization¹⁴ techniques. These methods rely on photoinitiation of azodiisobutyronitrile initiator at 360 nm wavelength, however. This is a region of the spectrum where both *o*-VBP monomer and polymer absorb, thus precluding quantitative photolysis of the initiator. In addition, the use of wide spectrum Hg lamps in these techniques means that the allowed $\pi-\pi^*$ transitions (Table 1) can occur and this would introduce the possibility of additional complex photochemistry. For these reasons, the separate rate constants were not measured for this polymerization.

The molecular weight distributions of the polymers made under controlled conditions are summarized in Table 3. These are all rather low molecular weight products. A high molecular weight polymer was not obtained in an isothermal polymerization and its characteristics are not recorded in this Table. Sample K₁ is the polymer made during the kinetic measurements summarized in Figures 3 and 4. Predicted conversions were obtained from equation (6) with the quoted value of $k_p/k_t^{1/2}$. Similarly, predicted \bar{M}_n values were estimated with equation (7) on the assumption that free radical termination was entirely by combination ($\bar{M}_n = 2v$). In general, both the conversion and \bar{M}_n values predicted with $k_p/k_t^{1/2} = 1.1 \times 10^{-2} \text{l}^{1/2} \text{mol}^{-1/2} \text{s}^{-1/2}$ agree reasonably well with experimental figures. The polydispersities (\bar{M}_w/\bar{M}_n) of low conversion samples P₁ and P₅ were 1.70 and 1.74, respectively. The \bar{M}_w/\bar{M}_n ratio would be 2.0 if termination of the growth of polymer chains were entirely by disproportionation or chain transfer and would be 1.5 if termination were entirely by combination of free radicals. The measured values suggest that the *o*-VBP radicals terminate by disproportionation as well as by coupling. This is in contrast to the case of polystyrene where termination is entirely by combination. This difference is as expected since the bulkier substituent in *o*-VBP may hinder formation of the transition state complex

Table 3 Molecular weight distributions of homopolymers of *o*-VBP

Sample	Predicted $\bar{M}_n \times 10^4$	Predicted conversion (%)	Experimental conversion (%)	$\bar{M}_n \times 10^4$	$\bar{M}_w \times 10^4$	$\bar{M}_z \times 10^4$	\bar{M}_w/\bar{M}_n	Molecular weight measurement*
K ₁	1.00	—	—	1.38				v.p.o.
P ₁	1.10	1.5	1.0	0.61	1.04	1.78	1.70	g.p.c.
P ₂	0.84	66	77	1.06	2.79	10.30	2.59	g.p.c.
					2.70 [‡]			l.s.
P ₃ †	—	—	>75	16.9	58.8	113.0	3.14	g.p.c.
				20.6				m.o.
P ₄	5.18	50	38	3.89	7.21	15.94	1.85	g.p.c.
P ₅	5.18	<1	<1	4.32	7.50	12.18	1.74	g.p.c.

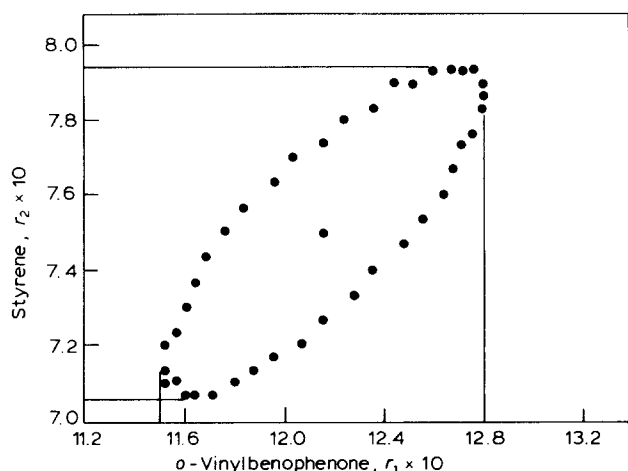
* g.p.c. = gel permeation chromatography in tetrahydrofuran; v.p.o. vapour-phase osmometry in tetrahydrofuran; l.s. = light scattering in toluene; m.o. = membrane osmometry in toluene

† Bulk polymerization

‡ $dn/dc = 1.4364 \times 10^{-4} \text{ l g}^{-1}$ (toluene, 25°C)

Table 4 Compositional data for the copolymerization of *o*-VBP and styrene

<i>o</i> -VBP (g)	Styrene (g)	AIBN (mg)	Yield (g)	<i>o</i> -VBP in feed (mol %)	<i>o</i> -VBP in polymer (mol %)
3.0034	3.0602	50.1	0.87	0.3292	0.3892
3.0612	3.0127	50.1	0.81	0.3369	0.3938
3.0237	3.0247	50.1	0.83	0.3333	0.3895
3.9999	1.2725	42.1	0.62	0.6111	0.6663
4.2180	1.0484	42.3	0.62	0.6680	0.7140
4.5325	1.1283	42.0	0.63	0.6676	0.7130

Figure 5 Confidence loop (95%) for reactivity ratios in *o*-VBP/styrene free radical copolymerization at 70°C

needed for termination by coupling. Polydispersities of high conversion polymers (P_2 and P_3 are greater than 2, presumably because of the gel effect, which would only be evident at fairly high conversions in solutions of low molecular weight polymers.

The unperturbed dimensions of poly(*o*-VBP) were estimated from intrinsic viscosity data in tetrahydrofuran using the extrapolation procedure of Chee¹⁵. Initially the Mark-Houwink pre-exponential constant for theta conditions, K_θ , is calculated from:

$$K_\theta = K\phi_0^{-(2a-1)/3}\alpha_1^{-\beta}N_1^{(2a-1)/2}$$

$$K_\theta = \left[K\phi_0^{-(2a-1)/3}(1.20)^{(2a-1)/4.25}\left(\frac{M_1}{L_1}\right)^{(2a-1)} \right]^{3/2(2-a)} \quad (8)$$

where ϕ_0 is Flory's universal constant, taken here as 2.87×10^{23} (with $[\eta]_\theta$ in $\text{cm}^3 \text{g}^{-1}$), K and a are the constants of equation (4) and M_1 is the molecular weight of a polymer with contour length l_1 . The ratio M_1/L_1 is 4.135 Daltons cm^{-1} for polystyrene^{16,17} and it is therefore double this value for poly(*o*-VBP) since the formula weight of the latter monomer is twice that of styrene. It follows that $K_\theta = 5.93 \times 10^{-2} \text{cm}^3 \text{g}^{-1}$. The ratio of unperturbed mean square end-to-end distance to molecular weight ($\bar{r}_0^2/M^{1/2}$) is calculated from:

$$(\bar{r}_0^2/M) = (K_\theta/\phi_0)^{1/1.5} \quad (9)$$

Then $\bar{r}_0/M^{1/2} = 0.59 \times 10^{-8} \text{cm}$. This compares to a value

of $0.67 \times 10^{-8} \text{cm}$ for polystyrene. The ratio of unperturbed dimensions of the actual and free rotating analogue chains is 2.2 for polystyrene¹⁸ and the same value for poly(*o*-VBP) is almost double, at 3.93. This is not surprising, in view of the bulk of the substituent in the latter polymer.

The copolymerization of *o*-VBP and styrene was carried out in bulk at 70°C for 20 min using azobis(isobutyronitrile) initiator. Copolymer composition was conveniently measured using quantitative i.r. analysis of the strong carbonyl band at 1665cm^{-1} . Composition data were confirmed for several samples using inverse gated ¹³C n.m.r. measurements. Initial experiments indicated that r_1 and r_2 , the reactivity ratios for *o*-VBP and styrene respectively, were close to unity. These estimates were used as input variables in the approximate design scheme reported by McFarlane and coworkers¹⁹, which was used to determine a pair of optimum feed ratios at which a number of experiments were to be run to measure reactivity ratios. The 'target' comonomer feeds contained 0.33 and 0.67 mol% *o*-VBP and three copolymerizations were performed under each of these conditions. The resulting data are shown in Table 4. Reactivity ratios were calculated from the simple copolymer equation²⁰ using the non-linear least-squares estimation procedure of Tidwell and Mortimer²¹. The reactivity ratios found were r_1 (*o*-VBP) = 1.216, $r_2 = 0.751$. Figure 5 shows the 95% confidence limit loop for these reactivity ratios. The r_1r_2 product is 0.91, which corresponds to virtually random copolymerization. This comonomer pair will not have an azeotropic feed composition.

EXPERIMENTAL

Preparation of *o*-vinylbenzophenone

The first step in the three-part synthesis of *o*-vinylbenzophenone involved the reaction of β -phenethylamine and benzoyl chloride in the presence of base. The following were placed in a 1.5 litre round-bottomed flask equipped with a condenser and mechanical stirrer: β -phenethylamine (104 ml, 0.82 mol), diethyl ether (300 ml) and 20% aq. NaOH (200 ml). Benzoyl chloride (100 ml, 0.825 mol) was added dropwise to the rapidly stirring mixture. After 2 h, the amide precipitate was dissolved in ethyl acetate and washed thoroughly with water. The solution was then dried over anhydrous sodium sulphate and pumped down under reduced pressure to give a 90% yield of the β -phenethylamide (m.p. 116–117°C).

Cyclization to 1-phenyl-3,4-dihydroisoquinoline was accomplished using a Bischler-Napieralski type reaction. The β -phenethylbenzamide (61 g) was added to a slurry of

phosphorus pentoxide (200 g) in phosphorus oxychloride (200 g) and dry xylene (400 ml). The mixture was stirred vigorously and was allowed to reflux under anhydrous conditions for 5 h. The reaction mass was then cooled and ice-water was carefully added to consume the excess dehydrating agent. The xylene layer was washed with small quantities of 1 N hydrochloric acid and the washings were then combined with the original aqueous layer. The aqueous mixture was made basic by careful additions of 30% sodium hydroxide. The 1-phenyl-3,4-dihydroisoquinoline formed as an oily layer on top of the mixture and was removed by repeated extractions with methylene chloride. This was dried over anhydrous sodium sulphate and pumped down under reduced pressure to leave 57 g of dark oil.

To effect the ring opening to the desired *o*-vinylbenzophenone, the 3,4-dihydroisoquinoline (30.0 g) was refluxed with water (280 ml), sodium hydroxide (120 g) and dimethylsulphate (60 ml) for 3 h at 80°–85°C. The product was extracted with ether and washed with 1% hydrochloric acid, 10% sodium carbonate and, finally, water. The ethereal layer was dried and pumped down to yield 25.8 g of red oil. Distillation under vacuum gave a pale yellow product. Samples of monomer were refrigerated under nitrogen atmosphere for long-term storage. The monomer had n_D^{20} equal to 1.6189 and b.p. of 114°–116°C at 0.55 mmHg pressure. The n.m.r. and i.r. spectra were consistent with the structure of *o*-vinylbenzophenone.

Kinetics of homopolymerization

The *o*-vinylbenzophenone monomer was distilled twice immediately prior to use and was pale yellow in appearance. The initiator, azobis(isobutyronitrile) (AIBN) was recrystallized twice from ethanol–water and once from cold methanol by evaporation. Spectrophotometric-grade toluene was used throughout.

The polymerization reaction was carried out in a 25 ml three-necked flask fitted with a rubber septum, a thermometer and a microcondenser with a rubber balloon attached. The flask was charged with toluene (10.0 ml), monomer (5.2 ml, 5.731 g) and AIBN (0.375 g). Purified nitrogen was bubbled through the solution for 10 min using a syringe needle inserted through the septum. A second needle acted as a vent. After purging, the vent needle was removed, allowing the balloon to fill with nitrogen. The nitrogen needle was removed, and the magnetically stirred flask was immersed in a 60°C bath. Samples (0.3 ml) were withdrawn periodically for gas chromatographic (g.c.) analysis of residual monomer²². In order to avoid difficult sample preparation, the g.c. column was fitted with a glass-wool plug to precipitate polymeric material at the injector. Samples were injected directly and monomer concentration was calculated by peak area as determined by disc integration. The toluene solvent peak was taken as an internal standard. G.c. measurements were made on a Carle 9000 gas chromatograph equipped with flame ionization detector. The column (8% dinonyl phthalate on Anakrom ABS) was held at

127° ± 1°C. After 20 h, the remaining reaction mass was precipitated in methanol, and dried *in vacuo* for 48 h. \bar{M}_n was measured in toluene by vapour-phase osmometry. Additional samples of poly(*o*-vinylbenzophenone) with varying molecular weight distributions were prepared under similar conditions. Initiator and monomer concentrations were varied to shift the average molecular weight of the product. In cases where long reaction times were necessary to achieve high molecular weight, AIBN levels were replenished on a daily basis.

Glass transition temperatures were measured on a Perkin–Elmer DSC-II. Polymer samples were first pressed into pellets then sealed into aluminium sample pans. Each sample was scanned at heating rates of 10, 20 and 40°C min⁻¹ through the glass transition temperature and was allowed to cool at 20°C min⁻¹ between scans. The glass transition temperature was taken as the position of the transition peak and was plotted vs. log heating rate to yield T_g as the intercept at log heating rate equal to zero²³.

ACKNOWLEDGEMENTS

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