A novel high-temperature non-aqueous dispersion polymerization route to fully aromatic main-chain liquid-crystal polymers

A. Bunn, B. P. Griffin, W. A. MacDonald* and D. G. Rance
ICI Wilton Materials Research Centre, PO Box No. 90, Wilton, Middlesbrough, Cleveland TS6 8JE, UK
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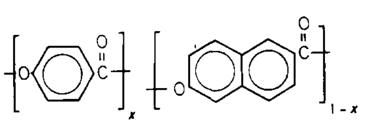
A novel high-temperature non-aqueous dispersion polymerization route to liquid crystal polymers based on poly(4-oxybenzoate-*co*-2,6-oxynaphthoate) is described. Novel combinations of polymeric and hydrophobic inorganic stabilizers are shown to give stable dispersions at temperatures up to 320°C. A possible mechanism of stabilization is discussed.

(Keywords: polymerization; liquid-crystal polymers; stabilization)

INTRODUCTION

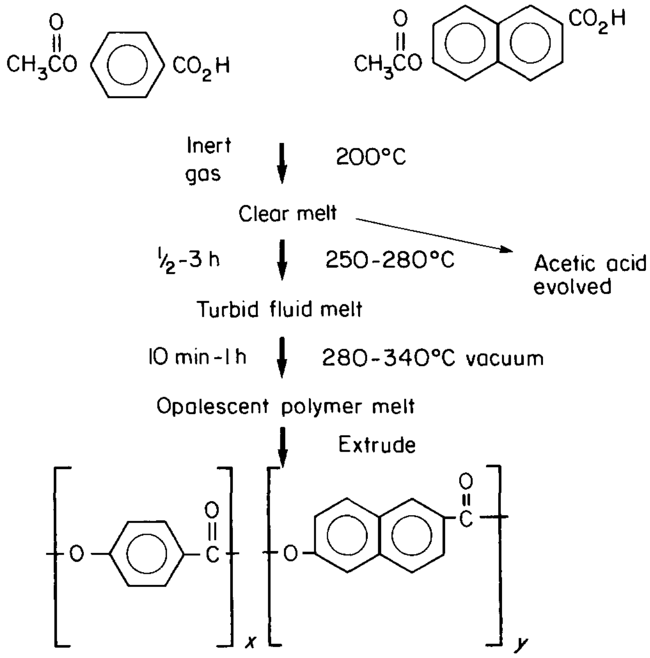
Most industrial main-chain thermotropic liquid-crystal polymers (LCPs) based on fully aromatic monomers are prepared by an ester exchange reaction between acetoxyaryl groups and carboxylic acid groups, with the elimination of acetic acid at a temperature above the crystalline melting point (T_m) of the polymer produced[1]. For example, in the preparation of poly(4-oxybenzoate-*co*-2,6-oxynaphthoate) (LCP-1) shown below, the



acetylated monomers are heated in an autoclave under a nitrogen atmosphere to 320–340°C, and once the majority of the acetic acid has been evolved, a vacuum is applied to the prepolymer to increase the molecular weight of the polymer (*Scheme 1*)[2]. Although LCPs have low melt viscosities at high shear rates, these aromatic polyesters have relatively high melt viscosities, compared for example with poly(ethylene terephthalate) (PET), under the low shear conditions of the autoclave. Furthermore, these aromatic LCPs can have relatively high melting points (>270°C to intractability). The upper limit therefore for the molecular weight of LCP polymers prepared by a melt condensation reaction is determined by the ability to extrude the polymer from a melt autoclave. This limitation becomes more severe as the value of T_m of the LCP rises above 300°C.

To overcome the problem that the viscosity of the melt polycondensation limits the molecular weight, one route has been to prepare a low-molecular-weight prepolymer by the melt route, followed by a subsequent solid-phase polymerization to complete the process[3]. Another route has been to prepare LCPs, in particular high-melting LCPs, in an inert heat transfer medium where the temperature of the stirred polymerization mixture is raised very slowly over a matter of hours to days, presumably to ensure that the temperature of the reaction slurry remains below the melting temperature for the polymer as its molecular weight increases[4,5]. Coarse granules consisting of smaller particles fused together are ultimately obtained.

The present authors have found, however, that in the preparation of polymers of the LCP-1 type in heat transfer media, if the temperature of the stirred mixture is raised quickly (from 200 to 300°C in ≈1–2 h),



Scheme 1 A typical melt acidolysis route to LCPs

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*To whom correspondence should be addressed

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flocculation of the granules occurs because of a lack of stabilization at the interface.

Stable dispersions of condensation polymers, e.g. PET, have been prepared by non-aqueous dispersion (NAD) polymerization techniques in organic media in the presence of polymeric dispersants, e.g. a graft copolymer based on poly(12-hydroxystearic acid), methyl methacrylate and glycidyl methacrylate in the weight ratio 10:9:1. Non-aqueous dispersion polymerization has been extensively reviewed elsewhere[6,7]. Essentially the polymeric dispersant is designed to have segments that are soluble in the heat transfer medium, in this particular example poly(12-hydroxystearic acid), and segments in the polymer backbone that anchor to the condensation polymer (the epoxy group in glycidyl methacrylate). The polymeric dispersant sits at the surface of the polymer droplet and prevents flocculation or coalescence by a mechanism of steric repulsion between segments of the dispersant that are soluble in the heat transfer medium. In this way, spherical particles in the size range 1–20 μm are normally achieved. With condensation polymers, the rate of reaction depends on the rate at which the by-product is removed from the reaction mixture. In an NAD polymerization the small particle size and high surface area of the droplets allows, in the example of PET, rapid removal of the by-product (ethylene glycol), with the result that the polymerization can be carried out 50°C below the normal melt polycondensation temperature.

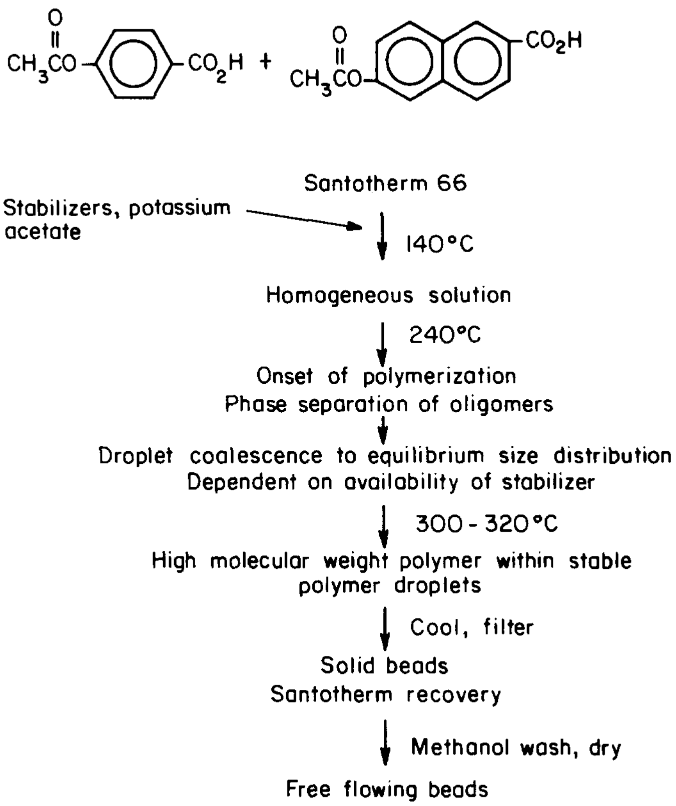
An NAD polymerization route to LCPs would obviously be attractive, as it would overcome the problem of the limitation of molecular weight by the viscosity of the melt, and would offer the possibility of carrying out the polymerization at lower temperatures. However, the NAD polymerization work discussed above for PET was carried out at $\approx 250°C$, and at this temperature the melt acidolysis reaction involving acetylated aromatic monomers, such as those used in the preparation of LCP-1 as shown in *Scheme 1*, is only just beginning as evidenced by the evolution of acetic acid. Furthermore, the graft polymeric dispersants mentioned above become increasingly thermally unstable above 250°C, precluding their use at 320°C. Novel thermally stable dispersants that would operate at the required polymerization temperatures for LCPs therefore needed to be developed. A programme of work to develop such dispersants was initiated in the authors' laboratory, and LCP-1 was used as the control polymer. Before the programme was begun, however, a suitable heat transfer medium had to be identified. The criteria used for selection were that the heat transfer medium should:

(1) be liquid at room temperature for ease of handling;
(2) have a boiling temperature greater than 340°C;
(3) be stable and inert.

Very few organic liquids meet these criteria, and Santotherm 66, a mixture of partially hydrogenated terphenyls, was selected.

On the basis of both experimental observation and existing knowledge, the following guidelines for designing a suitable polymeric dispersant were developed. The polymer should

(1) contain groups that might interact with the LCP;
(2) have a component that is soluble in the heat transfer medium;
(3) be random in sequence, with a statistical probability of blocks occurring and not be alternating or regular;
(4) be thermally stable in the heat transfer medium at >300°C.



Scheme 2 A typical non-aqueous dispersion polymerization route to LCPs

An acrylic copolymer based on methyl methacrylate (MMA), styrene, 2-ethylhexylacrylate, and acrylic acid (AA) in the ratio 0.4:0.4:0.1:0.1 was found to meet all these criteria.

In parallel with this work, potential inorganic stabilizers were evaluated, in particular hydrophobic silicas such as Aerosil R972. Although both the acrylic copolymer and the hydrophobic silica gave partial stabilization of LCP droplets in the initial stages of the dispersion polymerization, in both cases the dispersions flocculated before the polymerization was complete. It was discovered, however, that if the acrylic copolymer and Aerosil R972 were used together, an additive effect was obtained and a stable dispersion following the scheme outlined in *Scheme 2*, surviving up to 90 min at 320°C, was obtained.

This paper describes and discusses the novel NAD route and attempts to elucidate the mechanism of stabilization.

EXPERIMENTAL

Materials

Santotherm 66 was supplied by Monsanto and used without further purification. Aerosil R972, an 80% methylated silica of average particle size 16 nm, was supplied by Degussa. 4-Acetoxybenzoic acid and 2,6-acetoxynaphthoic acid were supplied by Ueno Fine Chemicals.

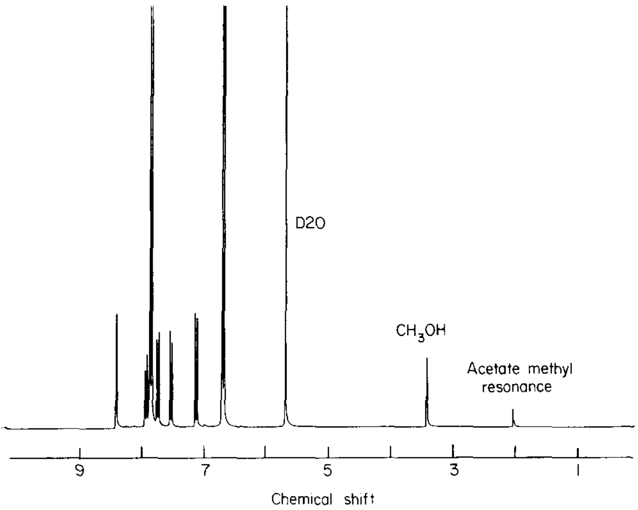


Figure 1 270 MHz ^{1}H n.m.r. spectrum of hydrolysed LCP-1

Acrylic copolymer preparation

A 5 litre glass flask was charged with demineralized water (2 litres), sodium lauryl sulphate (10 g), potassium persulphate (1 g), methyl methacrylate (220 g), styrene (200 g), 2-ethylhexyl acrylate (50 g), and acrylic acid (50 g). The monomers were polymerized at 60–65°C with stirring under a nitrogen blanket and then heat-treated at 90–95°C for 30 min. After cooling, the latex was poured into an equivalent volume of methanol to coagulate the acrylic copolymer. The mixture was heated to 90°C for 5 min with stirring and then cooled and filtered.

Typical dispersion polymerization

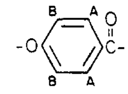
A 3 litre flanged reaction vessel, fitted with nitrogen inlet, thermometer (or thermocouple), Vigreux column ($\simeq$19 cm) attached to condenser and receiver vessel, and four-bladed impeller (10 cm diam. angled 60° to horizontal to give downthrust), was charged with 4-acetoxybenzoic acid (607.5 g, 3.375 mol), 2,6-acetoxynaphthoic acid (287.1 g, 1.248 mol), acetic anhydride (21.5 g, 2.4% on monomers), acrylic polymer (0.89 g, 0.1% on monomers), Aerosil R972 (2.47 g, 0.275% on monomers), potassium acetate (0.045 g, 50 ppm on monomers) and Santotherm 66 (895 g, 1:1 ratio with monomers). The mixture was then heated to 220°C over 60 min under nitrogen. The mixture was stirred gently initially ($\approx$100 rev min^{-1}), but the stirrer speed was increased to 450–550 rev min^{-1} once the monomers had melted to give a clear solution at $\approx$170°C. As the temperature of the medium was raised, distillate began to be evolved at $\approx$230°C and the temperature of the batch was raised to 320°C over $\approx$40 min with constant evolution of acetic acid (290 g, 97% evolved). Product precipitated from solution at $\approx$270°C. The reaction was held at 320°C for 30 min and the mixture was then allowed to cool. The product was filtered, washed twice with acetone (equivalent volumes) and dried under vacuum at 80°C to yield typically LCP-1 (592.6 g, 96%) as cream-coloured particles of size 10–210 μm (but mainly 140–210 μm) and melt flow index (MFI) 12–18 (10 kg at 310°C). Polymers of varying molecular weights could be prepared reproducibly by varying the polymerization time at 320°C.

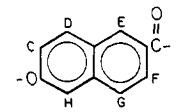
Molecular weight determination

Intrinsic viscosity (IV) measurements were carried out at 60°C in pentafluorophenol, and MFI measurements at 310°C using a 10 kg weight and a die of hole diameter 1.18 mm.

^{1}H n.m.r. end-group analysis

The basic procedure described by Kricheldorf and Schwarz[8] was used to determine acetate end-group concentrations. The polymer was hydrolysed at 50–60°C by means of a CD_3OD–D_2O–NaOD mixture ($\approx$12:3:1 by weight). ^{1}H n.m.r. spectra were taken on a JEOL FX270 spectrometer operating at 270 MHz. A typical spectrum is shown in *Figure 1* and an expansion of the resonances from the aromatic units in *Figure 2*, where the proposed assignments refer to the structures





Under the conditions of the hydrolysis the 'H' hydrogens are substantially deuterated and this results in decoupling of this resonance and the removal of the 'meta-coupling' between H_H and H_C. Thus the spectrum of hydrolysed polymer is different from the spectra of the monomers dissolved in the same solvent system (*Figure 3*).

For the spectrum shown in *Figure 1* the resonances from the acetate end group and, as appropriate, aromatic resonances were plotted on grid paper after expansion, and the areas were determined by summing the grid squares under each resonance. For high-molecular-weight polymers a ^{13}C satellite resonance from an appropriate aromatic resonance (usually H_B) was used so that the areas of the acetate resonance and the reference ^{13}C satellite would be approximately the same. This approach allows for the determination of M_n values if each polymer chain is assumed to have one acetate group per chain. As the aromatic resonance used for area measurement arises from only one of the

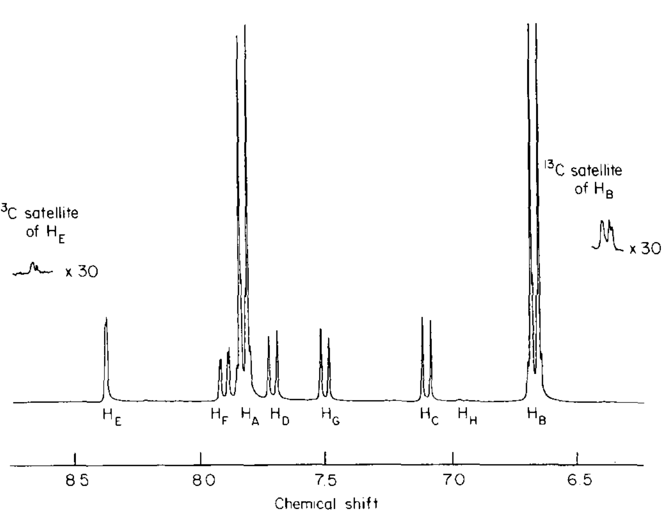


Figure 2 Aromatic region of the 270 MHz ^{1}H n.m.r. spectrum of hydrolysed LCP-1

non-ionic residues, the overall composition of the copolyester has either to be known or determined from the ^{1}H n.m.r. spectrum. In this work the latter method was used, the composition being determined from resonances from H_B and H_G:

$$\text{molar ratio}\left(\frac{\text{hydroxybenzoate (HBA)}}{\text{hydroxynaphthoate (HNA)}}\right)$$

$$=\frac{\left(\dfrac{\text{area of H}_B\text{ resonance}}{2}\right)}{(\text{area of H}_G\text{ resonance})}=K$$

$$\text{HBA (mol\%)}=\frac{K}{1+K}\cdot 100=K_1$$

$$\text{HNA (mol\%)}=\frac{1}{1+K}\cdot 100=K_2$$

M_n was calculated as follows. If the areas of the resonances from H_B and the acetate group are denoted by A_{HB} and $A_{acetate}$, then M_n is given by

$$M_n=\frac{A_{HB}/2}{A_{acetate}/2}\cdot\left(M_{HBA}+\frac{K_2}{K_1}M_{HNA}\right)\qquad(1)$$

where M_{HBA} and M_{HNA} are the molecular weights of the hydroxybenzoate and hydroxynaphthoate residues, taken as 120 and 170 respectively. If the ^{13}C satellite from H_B is used, and if $A_{HB,sat.}$ denotes the area of the ^{13}C satellite, then

$$A_{HB}=100A_{HB,sat.}/0.55$$

Light-scattering measurements on stabilizer systems

Stabilizer systems with a silica:acrylic ratio relevant to the suspension polymerization were stirred in Santotherm 66 at 600 rev min^{-1} and heated to 320°C. After this temperature had been maintained for 30 min, a sample was extracted by syringe and transferred to a cylindrical glass cell housed in a heated block at the centre of a table on a light-scattering photometer. After the sample had been allowed to equilibrate at 320°C for 10 min, light-scattering measurements at a wavelength of 546 nm were recorded as a function of scattering angle. The sample was allowed to cool slowly, and the angular variation in light scattering was recorded at different temperatures.

From photomultiplier counts corrected for solvent, the average size of the scattering units was obtained from Mie theory, using the measured dissymmetry and the refractive indices of Santotherm and silica at the relevant temperature.

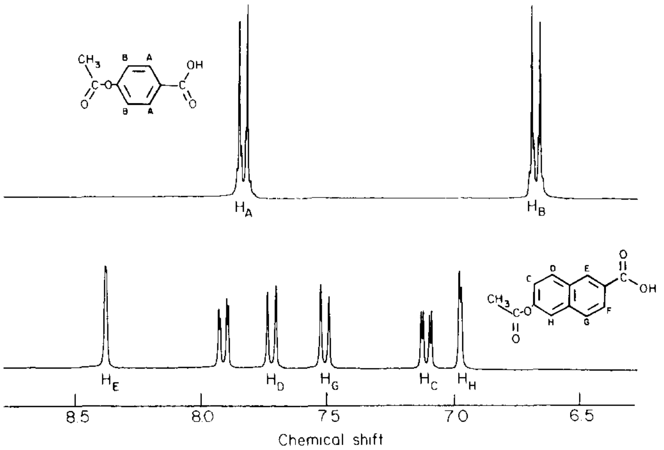


Figure 3 Aromatic region of the 270 MHz ^{1}H n.m.r. spectra of hydrolysed 4-acetoxybenzoic acid and 2,6-acetoxynaphthoic acid

RESULTS

Polymer characterization

Infra-red spectra of the LCP-1 prepared by the NAD route were compared with those of LCP-1 from the melt route. They showed that the ratio of the relative intensities of the bands at 1570 cm^{-1} (HBA unit) and 1470 cm^{-1} (HNA unit) were identical, i.e. the same ratio of HBA to HNA was present in both samples. Similarly, dynamic mechanical analysis, differential scanning calorimetry and X-ray crystallinity studies showed no differences between the samples.

Intrinsic viscosity measurements are recorded in *Table 1*. Because of the inconvenience of measuring IVs in pentafluorophenol, a simple melt flow index test was devised. Comparison of the various indications of molecular weight (IV, MFI, and n.m.r. end-group analysis) in *Table 1* shows reasonable correlation.

Table 1 Molecular weight *versus* mechanical properties for LCP-1 prepared by NAD and melt routes

				Flexural modulus (GPa)				
					Disc			
Sample	Melt flow index	Intrinsic viscosity (dl g^{-1})	M_n^{b}	Bar	0°C	90°C	Tensile strength (MPa)	Total impact energy (N m)
LCP-1 (NAD)								
(a)	0.41^{a}	–	79 000	10.3	8.2	3.2	96.6	5.75
(b)	0.64	12.9	–	13.0	10.55	2.9	202	22.8
(c)	1.75	–	22 000	13.4	11.05	3	222	22.7
(d)	7.8	–	–	12.9	11.2	2.7	251	19.4
(e)	24	9.1	–	12.2	11.0	2.8	223	20.7
(f)	29	7.9	18 800	12.8	11.0	2.7	217	18.8
(g)	208	5.7	7000	12.1	11.1	2.8	209	11.7
LCP-1 (melt, typical)	200	4–5	–	10.1	9.5	2.7	166	16.2

^{a}At 330°C; no flow at 310°C
^{b}By end-group analysis

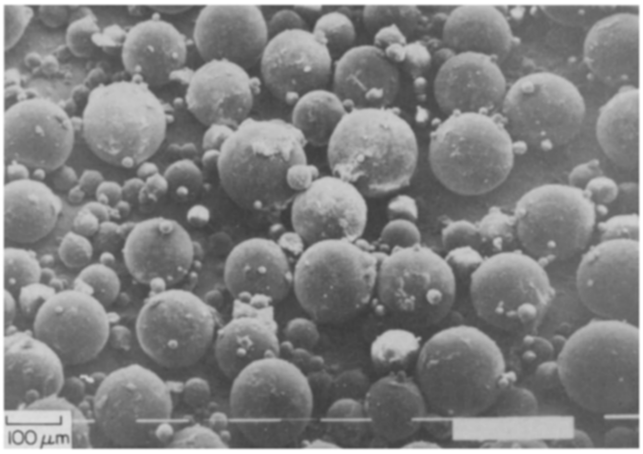


Figure 4 Electron micrograph of LCP-1 powder from NAD polymerization

Significantly, it is possible to obtain a much higher-molecular-weight product via the NAD route than via the melt acidolysis route. (Note that although high-IV polymer has been produced in small-scale glass polymerization equipment, it would be very difficult to discharge polymer of high IV effectively from an autoclave.)

Very good mechanical properties were obtained from injection-moulded tensile bars and discs of LCP-1 prepared by the NAD route over a range of MFI values (*Table 1*, LCP-1(a)–(g)). The flexural, tensile and impact properties deteriorated for the highest-molecular-weight polymer (LCP-1(a)). This is thought to be due to poor orientation of the very viscous melt during the injection moulding process. The mechanical properties of the polymer from the NAD route are superior to the average mechanical properties obtained for polymer from a melt.

Powder characterization

LCP-1 powder prepared under standard polymerization conditions as outlined under Experimental contained spherical particles of size 10–200 μm, as shown in *Figure 4*. Photon correlation light scattering gave median particle sizes of 115–145 μm. *Figure 4* shows that the particles have an essentially smooth surface but that patches of silica (identified by EDX) are present on the surface. Examination of the surfaces by both ESCA and SIMS confirmed that the silica was present within the surface region and also showed that the acrylic stabilizer was present at the surface of the polymer particles as either a discontinuous or very thin layer.

From measurements on a density column, the spherical particles were found to have a high density, 1.4 g cm^{-3}. The particles were uniformly of this density despite variation in particle size. LCP-1 extruded chip has a density of 1.36 g cm^{-3}, and LCP-1 films and fibres 1.4 g cm^{-3}, and the high density of the particles from the NAD route is believed to be due to lack of voids in the particles. There was no evidence that residual heat transfer medium was encapsulated in the particles.

Effect of stabilizer system composition and other reaction variables on particle size

Acrylic: Aerosil R972 ratio. See *Table 2*, series A. Initial studies were made using very high concentrations of acrylic stabilizer (1.6%) and Aerosil R972 (1.1%). This is an excessive level of stabilizer in relation to the available interface, as data from the light scattering experiments will show. The object of changing the acrylic:silica ratio was to optimize the NAD process at the minimum level of stabilizers. Subsequent analysis of the results revealed the following trends.

(1) For a given level of acrylic (A3, A4, A5 in *Table 2*), a reduction in the concentration of silica resulted in an increase in particle size until flocculation occurred.

(2) When the ratio of acrylic to silica was held approximately constant but the concentration of stabilizer was decreased (A2, A7, A8 in *Table 2*), the particle size increased until flocculation occurred.

(3) For a given level of silica (A3 and A6, A4 and A7 in *Table 2*), a reduction in acrylic concentration was accompanied by an increase in particle size.

Monomer: Santotherm 66 ratio. See *Table 3*, series B. Raising the monomer:Santotherm 66 ratio clearly provides an advantage in terms of yield per batch and hence overall productivity. However, the expected increase in droplet size on increasing the monomer: Santotherm 66 ratio from 1:1 to 1.25:1 eventually led to flocculation when an attempt was made to reach a ratio of 1.5:1.

Potassium acetate level. See *Table 4*, series C. Decreasing the potassium acetate level from 50 ppm to 25 ppm to zero produced an increase in particle size at each step.

Light-scattering measurements

Particle size data at different temperatures are shown in *Table 5* for 0.1% silica in Santotherm 66 and for 0.035% acrylic + 0.1% silica in Santotherm 66. The latter gives an acrylic:silica ratio of 0.35:1, which is the

Table 2 Effect of acrylic:silica ratio on particle size[a]

Code	Acrylic (wt% on monomer)	Silica (wt% on monomer)	Acrylic:silica ratio	Particle size of spheres (μm)
A1	1.6	1.1	1.4:1	110–300
A2	0.8	1.1	0.73:1	80–200
A3	0.4	0.275	1.45:1	40–90
A4	0.4	0.1	4:1	110–260
A5	0.4	0.0275	14.5:1	flocculated
A6	0.1	0.275	0.36:1	50–250
A7	0.075	0.1	0.75:1	175–350
A8	0.05	0.075	0.67:1	flocculated

[a] Monomer:Santotherm ratio 1:1; potassium acetate 50 ppm

Table 3 Effect of monomer:Santotherm ratio on particle size[a]

Code	Monomer: Santotherm ratio	Particle size of spheres (μm)
B1	1:1	35–175
B2	1.25:1	175–455
B3	1.5:1	flocculated

[a] Acrylic 0.1 wt% on monomer; silica 0.275 wt% on monomer; potassium acetate 50 ppm

ratio favoured for optimum suspension polymer properties.

Meaningful particle size data could not be obtained at 310–320°C, since there was almost perfect refractive-index matching between Aerosil R972 and Santotherm 66 at these temperatures. However, the data at lower temperatures are all completely consistent; the calculated silica particle size in Santotherm 66 is 184 nm (the average particle size of Aerosil R972 is 16 nm) and the particle size does not appear to be influenced by temperature or by the presence of the acrylic (this was also confirmed for 0.1% silica + 0.15% acrylic in Santotherm 66).

DISCUSSION: PROPOSED MECHANISM OF POLYMERIZATION AND STABILIZATION

Previous work on the synthesis of poly(4-oxybenzoate) by a slurry process has shown that the initially soluble monomers undergo polymerization to give soluble oligomers which at a certain degree of polymerization (DP $\approx$ 6–8) precipitate from the heat transfer medium[8]. It was also observed that if the oligomers were isolated from the heat transfer media, washed and reheated in fresh heat transfer medium, the polymerization would continue, showing that polymerization takes place within the particle droplets rather than depending upon the conversion of dissolved monomers. It is believed that the polymerization of LCP-1 proceeds by a similar route; indeed, if the droplets are isolated from the heat transfer medium and then redispersed in fresh heat transfer medium, polymerization will continue.

The initial product precipitates from solution in very fine-particle form ($<10\,\mu$m) and droplet coalescence occurs until an equilibrium size distribution dependent on the availability of stabilizers is achieved.

Neither the silica nor acrylic stabilizers on their own were sufficient to confer adequate stability on the suspension droplets. Aerosil R972 is an 80% methylated silica, hence the particle surface has a low surface free energy (≈ 30 mJ m^{-2}). Under these circumstances the silica is not completely wetted by either Santotherm 66 or LCP-1, and therefore an energetically favoured position for the silica particles is at the interface. It is proposed that the silica particles sit on the surface of the droplets and provide a physical barrier to coalescence.

However, it appears that such small particles cannot adequately maintain droplet stability, particularly at the stage when the viscosity of the droplets increases very rapidly. This is always the most crucial stage for droplet stability, by inference from the aqueous suspension polymerization of both acrylics and PVC. The presence of the acrylic stabilizer anchored at the interface is important at this stage during NAD, presumably to provide a harder repulsive interaction between suspension droplets. It is proposed that the AA–MMA segments are absorbed on the LCP-1 by rejection anchoring, while styrene segments remain soluble in Santotherm 66, and that the polymeric stabilizer acts by raising the interfacial viscosity of the particles to make it more difficult for them to deform, rather than by steric stabilization (i.e. a true colloidal dispersion is not achieved). (If the agitator is stopped, the particles sink to the bottom of the flask.) The presence of both silica and acrylic polymer at the surface of LCP-1 particles has been confirmed by ESCA. If the silica content is reduced below 0.275%, complete coverage of the interface can be obtained only by increasing the size of the droplets, but above a certain size (400–500 μm), stability cannot be maintained and flocculation ensues. It is not understood why beads of larger particle size are not possible when using limited stabilizer concentrations.

The high concentration of silica (1.1%) with a large excess of acrylic (1.6%) might be expected to give suspension droplets of small particle size, since the silica particle numbers are high, giving the possibility of stabilizing more interface. However, the observation that the suspension droplet size remains large may suggest that the silica is not reaching the interface. This might be because the acrylic is absorbed on to the silica and produces a completely stable silica dispersion with no driving force to seek the interface.

The effect of increasing the monomer:Santotherm 66 ratio, leading to a larger droplet size and eventually to flocculation, is exactly in line with expectation, because of the increased collision frequency between polymer droplets as the concentration of the disperse phase increases. Also of interest are the results for series C in *Table 4*: a reduction in the potassium concentration causes an increase in droplet size. This underlines the effect of potassium ions as a nucleant for precipitated material and the effect of initial nucleation density on the resulting droplet size distribution.

Table 4 Effect of potassium acetate level on particle size[a]

Code	Potassium acetate (ppm)	Particle size of spheres (μm)
C1	50	35–175
C2	25	175–245
C3	0	250–455

[a] Acrylic and silica contents as in *Table 3*; monomer:Santotherm ratio 1:1

Table 5 Light-scattering measurements in Santotherm 66

System	Temperature (°C)	I_{40}/I_{140}	Particle radius (nm)	I_{60}/I_{120}	Particle radius (nm)
0.1% Silica	230	2.87	76	2.62	91
	180	4.93	92	2.80	94
	140	5.51	92	2.82	93
0.1% Silica + 0.035% acrylic	230	5.12	94	2.49	90
	180	5.76	97	2.57	90
	140	5.87	96	2.71	91

CONCLUSIONS

Polymers based on poly(4-oxybenzoate-*co*-2,6-oxynaphthoate) can be successfully prepared by a high-temperature non-aqueous polymerization process with Santotherm 66 as the heat transfer medium, in which the polymer droplets are stabilized by the presence of (1) a copolymer based on methyl methacrylate, styrene, 2-ethylhexylacrylate and acrylic acid in the ratio 0.4:0.4:0.1:0.1 and (2) a hydrophobic silica, Aerosil R972. The polymerization, unlike melt polycondensation, is not limited by the viscosity of the melt, and high-molecular-weight polymers can be effectively obtained. Both the polymeric stabilizer and the hydrophobic silica are located at the surface of the particles, but neither alone gives complete stabilization. The silica forms a close-packed layer at the polymer–Santotherm 66 interface, but it appears that the silica alone cannot maintain droplet stability, particularly at the stage when the viscosity of the droplets is rising rapidly. It is proposed that the acrylic stabilizer has a compensating action, raising the interfacial viscosity of the particles and thereby making it more difficult for them to deform.

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