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High temperature non-aqueous dispersion polymerisation of aromatic main chain liquid crystal polymers using organo-clay stabilisation

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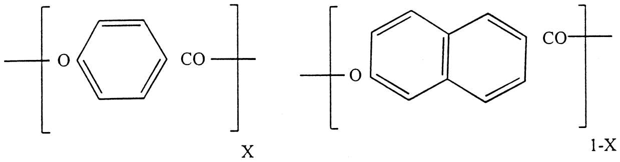
Abstract

A high-temperature non-aqueous dispersion polymerisation (NAD) route to poly(4-oxybenzoate-*co*-4-phenylene isophthalate) liquid crystal polymers (LCP) is described. Stable dispersions were obtained in the presence of organo-clay stabilisers. The use of organo-clay stabilisers is discussed and the advantages of the NAD route are contrasted with traditional melt polycondensation routes. © 1999 Elsevier Science Ltd. All rights reserved.

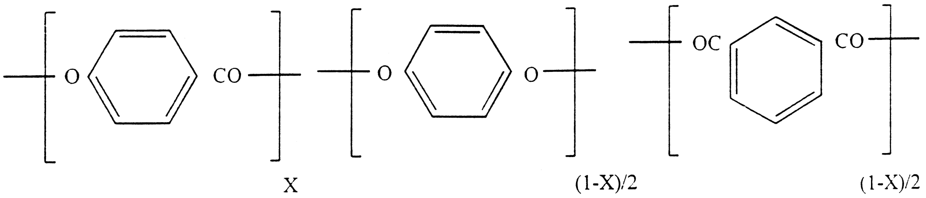
Keywords: Polymerisation; Liquid crystal polymers; Stabilisation

1. 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 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) shown later, the acetylated monomers are heated to 320°C–340°C in an autoclave under a nitrogen environment. Once the majority of the acetic acid was evolved, a vacuum is applied to the prepolymer to increase the molecular weight of the polymer [2].



Although LCPs have low 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. Further, these aromatic LCPs can have relatively high melting points ($>$ 270°C to intractability). The upper limit, therefore, for the 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 Tm of the LCP rises above 300°C, for example with polymers of the family based on poly(4-oxybenzoate-*co*-4-phenylene isophthalate) shown later.



One route taken to overcome the problem of the viscosity of the melt polycondensation limiting molecular weight was to prepare a low-molecular weight prepolymer by the melt route, followed by a subsequent solid-phase polymerisation to complete the process [3]. Another route was to prepare LCPs, in particular high-melting LCPs, in an inert heat transfer medium where the temperature of the stirred polymerisation mixture is raised very slowly over a matter of hours to days [4,5]. However, both these routes are time consuming and therefore costly. More recently, a novel high temperature non-aqueous dispersion route (NAD) to LCPs has been described [6].

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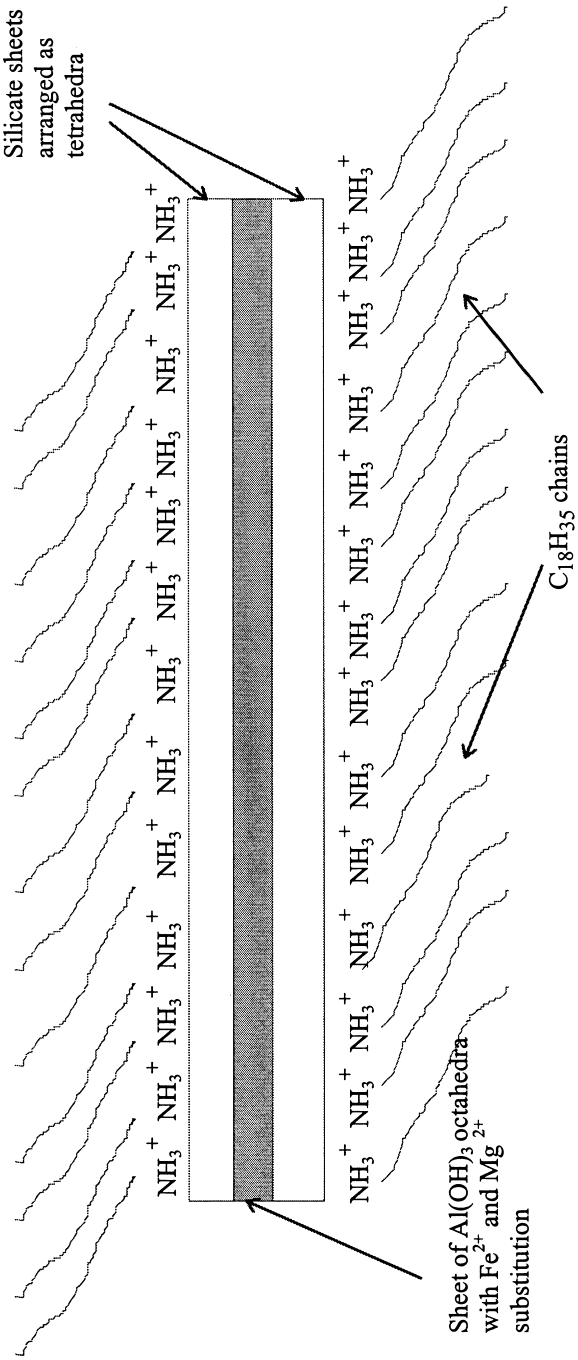

Fig. 1. Structure of a single platelet of organo-cation exchanged bentonite.

Fig. 2. Scanning electron micrograph of hectorite lamellae. (Reproduced with permission from ICI Plc.)

NAD polymerisation involves carrying out polymerisation reactions in an organic heat transfer medium in the presence of a suitable stabiliser. Stable dispersions of condensation polymers, e.g. PET were prepared by NAD 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. These NAD reactions were extensively reviewed elsewhere [7,8]. 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 glyciidyl 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. Spherical particles of size 1–20 μm are normally achieved and the rapid removal of the by-product of the polycondensation reaction, ethylene glycol in the case of PET, means that the polymerisation can be carried out at temperatures significantly below the normal melt polycondensation temperature.

An NAD polymerisation route to LCPs is attractive as it

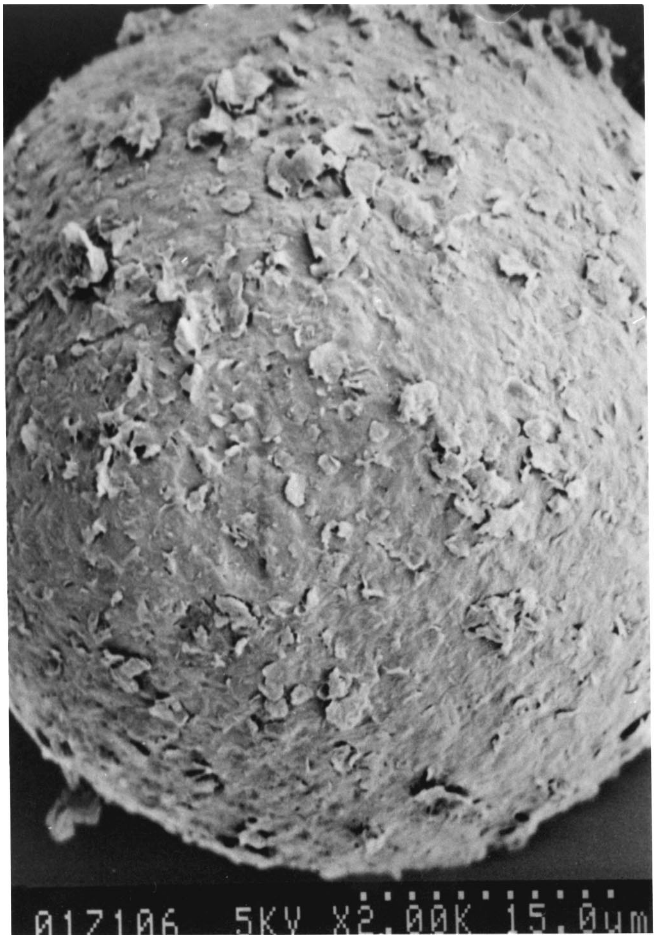

Fig. 3. Scanning electron micrograph of polymer particle at the end of polymerisation. (Reproduced with permission from ICI Plc.)

Table 1
Elemental analysis of organo-clays

Clay	%Carbon	%Nitrogen	%Hydrogen	%Chloride
A. $C_{12}H_{25}NH_3^-$ Bentonite	16.33	1.37	3.54	None detected
B. $C_{18}H_{35}NH_3^+$ Bentonite	21.61	1.26	1.44	< 0.3
C. $(C_{18}H_{35})_2Me_2N^-$ Vermiculite	34.87	1.16	6.91	0.5
D. $C_{18}H_{35}\cdot Me_2\cdot C_6H_5\cdot CH_2\cdot N^+$ Vermiculite	27.23	1.49	5.73	None detected
E. $(C_{18}H_{35})_2Me_2N^-$ Bentonite (Claytone 40, English China Clays Ltd.)	32.1	5.21	1.04	0.1
F. $(C_{18}H_{35})_2Me_2N^+$ Hectorite (Bentone 38, NL Chemicals)	27.9	0.8	5.2	0.1

overcomes the problem of the limitation of molecular weight by the viscosity of the melt, and would offer the possibility of carrying out the polymerisation at lower temperatures. This becomes even more important with higher melting LCPs. It was previously observed [6] that the polymeric stabilisers based on poly(12-hydroxystearic acid) were not stable at temperatures over 250°C for long periods of time, the temperature at which the melt acidolysis reaction is only just beginning. Both a suitable heat transfer medium and a thermally stable dispersant had to be identified. The criteria for selection of a suitable heat transfer media was that it should be:

1. liquid at room temperature;
2. have a boiling temperature greater than 340°C;
3. be stable and inert.

The criteria for the selection of a thermally stable heat transfer medium and thermally stable dispersant was described. In addition, a novel NAD route to poly(4-oxybenzoate-*co*-2,6-oxynaphthoate) using Santotherm 66, a mixture of partially hydrogenated terphenyls, as the heat transfer medium and a synergistic combination of an acrylic copolymer and Aerosil R972, a hydrophobic silica supplied by Degussa, was described. However, although this combination of organic and inorganic species was demonstrated to be successful as a dispersant system in NAD polymerisations for this specific liquid LCP formulation and heat transfer medium, this dispersant system, although meeting the temperature stability requirement for that polymerisation, was not versatile enough to be used when the chemical composition of the polymer was varied, in particular for the family of polymers based on poly(4-oxybenzoate-*co*-4-phenylene isophthalate). The mechanism proposed for that stabilising effect was that both the polymeric dispersant and the silica particles sit on the surface of the polymer droplet, but that neither alone gave complete stabilisation. It was postulated that the silica formed a closely packed layer at the polymer-Santotherm 66 interface, but that the silica alone could not maintain droplet stability, particularly at the stage when the viscosity of the droplets was rising rapidly. It was believed that the acrylic stabiliser compensated for that lack by raising the interfacial viscosity of the particles thereby making it more difficult for them to deform. On the basis of the understanding developed with this dispersant system, other inorganic species which could potentially provide physical barriers to coalescence were examined with the objective of finding a dispersant which could be used more universally at high temperature with a variety of polymer compositions. It was recognised that there was an analogy between the structure of the graft co-polymeric stabiliser and the structure of an organo-cation exchanged clay (see Fig. 1), in that both species have a flexible chain component that can be modified to be compatible with a dispersing medium. The nature of the organo-cation can be changed to incorporate both aliphatic and/or aromatic species. Thus the interaction of the organo-clay with the dispersing medium can be varied. Further, high aspect ratio clay platelets can be seen, from a theoretical basis, to possess physical features attractive in this application. Organo-cation exchanged clays were therefore investigated in more detail.

2. Organoclay stabilisers

To produce high aspect ratio organoclay platelets for in this application, two steps are required in the treatment of the clay minerals namely; ion exchange followed by expansion in organic solvent and dispersion to form a colloid.

As the primary particle size of hydrophobic silica, R972, is of the order of 16 nm, natural clay particles are usually much coarser with their lateral dimensions ranging from a few microns to several hundred microns depending on the clay morphology. In colloidal suspension in water however, clay particles $< 2\ \mu m$ can be isolated and used for cation exchange. Synthetic clays, Laponites (Laporte) are also available and because of their preparation by precipitation and hydrothermal treatment, the primary particles may be as thin as 1 nm. In this paper, only the exchange reactions of the naturally occurring clays are discussed.

Organo-cationic exchange reactions were extensively reviewed in the literature [9,10] where it can be seen that long chain quaternary ammonium cations may be used to replace the inorganic cations. The important features of exchange reactions are the extent of exchange, and the residual, inorganic cation and anion. The organophilic nature of the cation affects the compatibility of the resultant organo-clay with particular organic phases and also affects the degree of dispersibility of the clay. There is also an influence on these factors from the particle shape and size of the clay mineral employed. It is known from previous studies that bentonite platelets are equidimensional whilst hectorite platelets are elongated or lath shaped. The theoretical hectorite surface area is 20 times greater than that of bentonite and this is obviously important in the stabilisation process being discussed here. However, hectorite platelets are difficult to separate because of the higher van der Waal's attractive forces existing between the natural occurring clay platelets. In the case of all expanding lattice clay minerals, individual platelets as thin as 6 Å can be generated although lamallae consisting of 10–100 or greater individual layers are the norm (see Fig. 2). However, once a well-dispersed hectorite was produced then that clay has a superior surface area, for example, bentonite. Organophilic clays can be delaminated to give high surface area dispersions in organic solvents by a combination of chemical and mechanical means. The effect of the cation on clay dispersibility in various liquids was reported [11].

Talc is an example of a non-swelling clay as there are no exchangeable inorganic cations on the basal planes of the clay lamallae. Such exchangeable cations, present in expanding lattice minerals, are necessary to counterbalance a net overall negative charge within the clay platelet. Their presence is important to the approach described in this study. The exchange process should not be confused with the technology that renders the surface of a clay organophilic by coating with some organic species, calcium stearate, for example. These latter materials were examined as polymerisation stabilisers and were found to be ineffective. Although the organic coating has the effect of making the clay suitable (e.g. kaolin) as a compatibilised filler in polymeric matrices, there is only physical interaction of the organic component with the inorganic particle.

The ionic bond present between the organic species and the platelet surface is an important feature of the organo-cation exchanged clay stabilisers in that the organic species substantially remains attached throughout the NAD polymerisation; this is not the case where only a physical interaction exists between the clay platelet and the organic species [12].

3. Experimental

Isophthalic acid was supplied by Amoco, 4-hydroxy benzoic acid and 6-hydroxy napthoic acid by Ueno Fine Chemicals and 1,4-hydroquinone by Rhone Poulenc.

3.1. Preparation of organo-clays as stabilisers

On evaluation of the commercially available organo-clays, a further series was prepared in the laboratory to assess the nature and quantity of organo-cation that would be needed for a successful stabilisation process in a NAD polymerisation (see Table 1).

3.2. Cationic exchange process

Eighty grams of natural Wyoming bentonite clay was used for the preparation of the organo-bentonite derivatives. On each occasion, 3 l of 2 wt.% bentonite ($< 2\ \mu m$ particle size), dispersed in de-ionised water, was required. The clay was added slowly to water with high shear mixing. After leaving overnight, the coarser particles in the mix sedimented and the $< 2\ \mu m$ fraction remained in suspension which could then be decanted off, ready for use. There was some swelling of the natural sodium bentonite in water, which opens up the lattice. To this suspension was added, with shear mixing, an aqueous solution of the organocationic salt, the chloride, in a three fold excess necessary to satisfy the cationic exchange capacity of the clay. By using an excess, the replacement of a high proportion of the sodium cations by the organo-cation can be ensured. (Clays A and B). The particular bentonite employed had a theoretical exchange capacity between 80–100 meq/100 g. In the preparation of Clays, C and D, methanol was used to solubilise the quartenary salt, dimethyl dihydrogenated tallow ammonium chloride, approximating to $(C_{18}H_{35})_2Me_2N^- Cl^-$, (Arquad 2HT-75, Akzo-Chemie) prior to addition to the dispersed clay in water with stirring, as well as with dimethyl hydrogenated tallow benzyl ammonium chloride, $(C_{18}H_{35})\ Me_2\ CH_2C_6H_5N^+Cl^-$, (Arquad DMHTB-75). When vermiculite (cation exchange capacity 120–130 meq 100 g) was used (Clays C and D), it was necessary to initially prepare an intermediate sodium exchanged material, which swells considerably in water thus facilitating access of the bulky quarternary organo-cation to the exchangeable sites. The modification of vermiculite to an organo-clay is well documented [13]. After addition of the quaternary salt, stirring was further continued for an hour at room temperature, after which the clays were filtered, washed with water (or waterndash;methanol) until no chloride ion was present in the washings. The organo-clay was allowed to dry on a large filter paper at room temperature in an attempt to avoid aggregation. However, it was necessary to ball mill the clay so that material was less than 40 μm prior to the chemical and mechanical delamination procedure to aid dispersion in organic media.

The organic content (wt.%) of the experimentally prepared and commercial clays are shown in Table 1.

3.3. Maximising clay surface area

The organo-clay surface area available for stabilising the polymer droplet can be increased significantly by high shear milling to delaminate the platelets in the organic heat dispersing medium, which in this exercise was liquid paraffin. It has long been appreciated [14] that the presence of polar organic molecules such as acetone or methanol leads to swelling of the platelets and so the milling becomes more efficient in generating thinner platelets when these species are added. It is thought that the organic species migrate to the inorganic surface, increasing the basal spacing which in turn leads to more efficient delamination of the clay by high shear milling. Propylene carbonate was the preferred activating species used in this evaluation.

3.4. Evaluation of clay dispersion

Initially, high levels of stabiliser were used (5 wt.% with respect to monomers) to ensure that the exchanged clays could be given sufficient opportunity to work as stabilising moieties. The surface areas, and hence the number of stabilising particles per unit volume, were maximised before addition to the polymerisation by high shear milling in liquid paraffin (10 wt.% clay with respect to weight of paraffin) and swelling with propylene carbonate as described in the previous section.

Small-scale reactions based on a total of 100 g of monomers were used to evaluate the efficiency of the stabilisers in an NAD polymerisation.

3.5. A Typical non-aqueous dispersion polymerisation

A 700 ml round bottom flask equipped with nitrogen inlet, thermocouple, vigreux column attached to a condenser and receiver vessel, four bladed impeller (angled at 60° to the the horizontal) was charged with acetoxynaphthoic acid (32.09 g, 0.13 mol), acetoxy benzoic acid (67.91 g, 0.377 mol), acetic anhydride (2.4 g) and potassium acetate (0.005 g, 50 ppm on monomers). The mixture was heated to 230°C with slow stirring (100 rpm) and nitrogen flow (300 cm^3/min) over 45–55 min, at which stage acetic acid was beginning to be evolved. The organo-clay (5 g) in paraffin (100 g, 1 : 1, paraffin to monomers) was added at this stage and the stability of the polymerisation observed.

Small-scale polymerisations were also carried out to find the minimum weight percent of clay stabiliser that could be used effectively in the polymerisation. When greater quantities of polymer were required for characterisation, a 3 l vessel was used. A typical experiment at this scale is described later.

A 3 l flanged flask reaction vessel equipped with a nitrogen inlet, thermocouple, vigreux column (approximately 19 cm) attached to a condenser and receiver vessel, four bladed impeller (10 cm diameter), angled at 60° to the horizontal to give downthrust, was charged with 2,6-hydroxynaphtholic acid (13.58 g, 0.072 mol), *p*-hydroxy benzoic acid (358.69 g, 2.596 mol), hydroquinone (250.33 g, 2.272 mol), isophthalic acid (377.56 g, 2.272 mol), acetic anhydride (772.6 g, 7.574 mol) and potassium acetate (0.12 g). The contents of the flask were heated to reflux (147°C) over a period of 15 min with stirring (300 rpm). Reflux was maintained for 100 min. After this time the reflux condenser was replaced by a vigreux column (30 cm) and distillation apparatus. A nitrogen purge (100 cm^3/min) was applied to the flask, the temperature of the contents increased to 190°C over a period of 30 min and 375 ml of acid–acetic anhydride distillate collected.

At the same time as the previous acetylation was being carried out, the dispersion medium was prepared in a 5 l round bottom, flanged flask fitted with a nitrogen inlet, stirrer, thermocouple and distillation apparatus containing a 30 cm vigreux column. The dispersion medium consisted of liquid paraffin (BDH/WOM 14), 1130 g, into which was mixed 196 g of an organo-clay gel (1 part organoclay in 9 parts liquid paraffin).

A nitrogen purge was applied to the dispersion medium which was heated to 170°C with stirring (400 pm). The gel was produced by the technique described previously in this section by a combination of high shear milling using a Hobart mixer (model VCM 40) and activation by addition of polar solvent. 18 kg of liquid paraffin and 2 kg of organoclay were homogenised using slow stirring for 1 min prior to high shear mixing at full speed for a period of 20 min. 500 g of propylene carbonate was then added at slow speed and the dispersion gelled using full speed mixing over a period of 20 s.

The transfer tube was heated to 140°C and the acetylated monomers were transferred when they reached 190°C, from the 3 l flask to the 5 l flask, the proportion of organoclay with respect to the acetylated monomer was 1.5–5 wt.%. The contents of the flask were heated to 300°C over a period of 75 min. Distillate from the polymerisation reaction started to come over at 220°C–230°C. At 300°C a ‘sparge’ tube was inserted into the reaction and a nitrogen flow of 1000 cm^3/min applied. Reaction was continued for 100 min. The batch was filtered in ‘Genklene’, filtered, re-slurried in acetone, filtered again and dried.

3.6. A Typical melt polymerisation

A 1 l three necked flask, fitted with a paddle stirrer, vigreux column, distillation head attached to a condenser and receiver vessel, and an nitrogen inlet was charged with 4-acetoxybenzoic acid (226.2 g, 1.257 mol), isophthalic acid (182.5 g, 1.1 mol), 1,4-hydroquinone diacetate (213.3 g, 1.1 mol), 2,6-acetoxynaphthoic acid (8.3 g, 0.035 mol), potassium acetate (0.08 g, 133 ppm) and acetic anhydride (15.1 g, 2.4%). The flask was raised in temperature in the following manner:

1. held at 260°C until 55%–60% of the theoretical distillate was evolved;
2. held at 280°C until 85%–90% of the distillate was evolved;
3. held at 320°C for 40 min;
4. held at 340°C for 40 min.

The vigreux was removed and a ‘soft’ vacuum was applied. The vacuum was gradually increased to 1 mm or better and the polymerisation was continued until the

Table 2
Effectiveness of organo-clays as stabilisers for NAD polymerisations

Organoclay	Swelling/viscosity rise	Effective stabilisation?	Polymer colour
Clay A	Limited	No	–
Clay B	Limited	No	–
Clay C	Better than A,B	Yes	Brown
Clay D	″	Yes	Light brown
Clay E	Considerable increase	Yes	″
Clay F	″	Yes	Cream

polymer was too viscous to stir. The polymer was allowed to cool under vacuum.

3.7. Polymer characterisation

Intrinsic viscosity (IV) measurements were measured in a 30/70 (v/v) mixture of trifluoroacetic acid and dichloromethane [15] at 25°C. Transition temperatures were measured on a Perkin Elmer DSC-2 scanning at a rate of 20°C/min. The values quoted are for the reheat scans. The $T_m$was measured as the end point of the endotherm and the T_g was obtained by taking the value of the extrapolated onset.

4. Results and discussion

4.1. Organo-clay selection

At the milling stage all the clays, when being evaluated as potential NAD stabilisers, showed some compatibility with the liquid paraffin polymerisation medium. There was, however, only limited swelling even after addition of propylene carbonate, inferred from the observed small increase in viscosity of the mix, in the cases of Clays A and B. However, Clays C and D showed marked rises in viscosity, suggesting a high degree of delamination.

Using Clay A, there was initial dispersion of the monomer droplets but the suspension quickly became unstable and flocculation resulted. Clay B showed improved efficiency of stabilisation when it was added to the polymerisation flask and the condensation reaction progressed further. However, as the temperature of the reaction approached 300°C, flocculation was again observed.

Clays C and D both stabilised the polymersation through the polymerisation temperature range up to 320°C and the reaction was held at this temperature for 1 h. Despite successful stabilisation, the resulting polymers were very discoloured. Vermiculite is a mineral with, generally, a relatively high iron content compared to other clays. It was concluded that there had been some extraction of the metal from the clay by acetic acid during the polymerisation. As a consequence, vermiculite exchanged stabilisers were not studied further. However, there was clearly an advantage in using dimethyl dioctadecyl cation exchanged minerals for good stabilisation and the two commercial clays, Clays E and F were fully investigated with the objective of minimising the percentage of clay required for stabilisation. Although E could be used successfully, even at low clay stabiliser levels (1.5%), the improved product colour resulting from the use of stabiliser Clay F, an hectorite (at a similar low level) made it the choice for larger scale polymerisations. Table 2 summarises the results of the investigation.

4.2. Stabilisation mechanism

A scanning electron micrograph (SEM) of hectorite platelets, delaminated mechanically and chemically, is shown in Fig. 2.

The ability of the inorganic clay platelet to reside on the surface of the dispersed phase and to remain there requires some physical interaction in the same fashion as its polymeric equivalent, and how this may occur is not immediately apparent as anchoring sites on the clay platelet surface appear limited because of the close packed nature of the organo-cations. Even at the edge sites, there are anions present hindering any platelet–particle interaction. In practice, there is strong interaction of the platelet with the polymerising dispersed droplet and we postulate that unexchanged sites become available after delamination by chemical and mechanical means thus enabling close polymer particle–clay platelet interaction.

The organic cation on the organo-clay can be chosen to suit the nature of the heat-dispersing medium. In this report, long-chain aliphatics on the organo-cation were used for compatibility with liquid paraffin. The mechanism was shown to be similar to that of a polymeric stabiliser in that there is also a strong anchoring interaction between polymer particle and clay platelet. The anchoring sites appear to be generated during the milling process when unexchanged pristine inorganic surface is revealed. The theoretical representation of the hydrophobic clay shown in Fig. 1 may be idealised and it is likely that there are unexchanged available sites, inaccessible to the bulky organo-cation which, when exposed, would sterically bind to a polymer droplet. In this way the interaction would be unhindered by the presence of the organo-cation. The clay platelet thus resides at the polymer/liquid paraffin interface sterically preventing coalescence of the droplets even at temperatures >300°C. There is some degradation of the

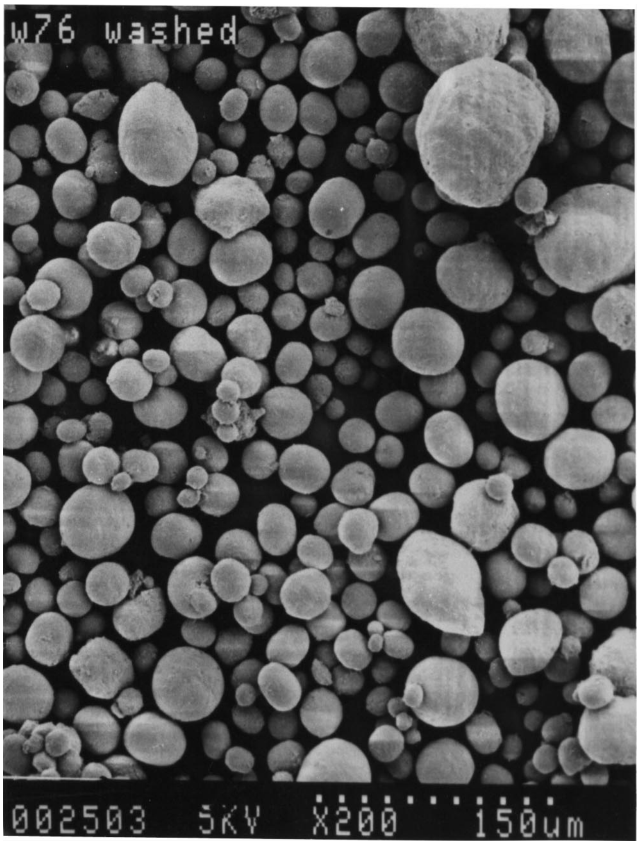

Fig. 4. Scanning electron micrograph of polymer particles after washing to remove excess clay. (Reproduced with permission from ICI Plc.)

organo-cation during the polymerisation but if sufficient is present at the critical phase of the polymerisation during molecular weight and viscosity increase then stabilisation can be successfully achieved. Fig. 3 shows a SEM of particles at the end of a polymerisation. There appears to be an excess of clay platelets on the surface of the polymer particles for dispersion but this may be necessary for protection. Excess clay can be removed from the polymer particles by washing in acetone and in chlorinated solvents which also removes the last traces of paraffin. Fig. 4 shows polymer particles after washing. The organo-hectorite ‘ Bentone 38’ was the preferred stabiliser because of its high organic content, its compatibility with liquid paraffin, high surface area after delamination and low iron content which resulted in a polymer with low colouration. This organo-clay stabiliser did prove to be more versatile than the silica and acrylic co-polymer dispersant system described in the Introduction using Santotherm as the heat dispersing medium [6] for polymerisations based on poly(4-oxybenzoate-*co*-2,6-oxynaphthoate) and poly(4-oxybenzoate-*co*-4-phenylene isophthalate).

Table 3
Effect of HNA content on the melting point of co-polymer

CODE	HBA	IA	HQ	HNA	T_m	T_g
(i)	27.5	36.25	36.25	0	336	136
(ii)	30	35	35	0	337	130
(iii)	36	32	32	0	334	127
(iv)	36	31.5	31.5	1	324	127
(v)	37.5	30	30	2.5	321	118
(vi)	40	30	30	0	335	119
(vii)	45	27.5	27.5	0	–	119
(viii)	50	25	25	0	–	114
(ix)	60	20	20	0	–	–
(x)	75	12.5	12.5	0	353	–

In fact, a wide range of polymers based on poly(4-oxybenzoate-*co*-4-phenylene isopohthalate) were successfully prepared by the NAD route involving organo-clays following the route described earlier. A representative family is shown in Table 3. In some cases, small levels of 2,6-hydroxy naphthoic acid were introduced into the formulation to depress the T_m and render the polymers more processable. The effect of the HNA on depressing the T_m can be seen in Table 3 with polymers (iv) and (v) relative to polymer (iii). No crystalline melting point was observed with polymers (vii) and (viii) containing 45%–60% HBA and no T_g process was observed with polymers (ix) and (x) containing 60% and 75% HBA. The thermal characterisation data is for illustrative purposes only as the characterisation and properties of this family of polymers was discussed more fully in other papers [15–19]. However, the significance of the T_ms is that polymers with high T_ms as discussed in Section 1 are difficult to prepare by standard melt acidolysis techniques and this problem becomes more severe as the Tm increases. If polymers of this type are prepared by a standard melt acidolysis route then it becomes increasingly difficult to reach high molecular weights without severely degrading the polymer. This is illustrated in Table 4 where the typical mechanical properties of polymer (iv) prepared by both the melt route and the NAD route are contrasted. The polymer made by the melt route had significantly lower molecular weight than the polymer achieved with the NAD route and although the stiffness of the two polymer types were similar the polymer made by the melt route was significantly more brittle than the polymer made by the NAD route which had a much higher tensile strength. This improvement in strength that can be achieved through the higher molecular weights attainable by NAD polymerisation were observed in the previous paper on NAD [6]. Further, the NAD polymerisation was carried out at 40°C lower in temperature than the melt polymerisation and whereas the NAD derived polymer was cream in colour, the melt made polymer was brown. The higher melting members of the poly(4-oxybenzoate-*co*-4-phenylene isophthalate) family such as polymer (x) are extremely difficult if not impossible to prepare by standard melt acidolysis routes, but were prepared using standard NAD polymerisation conditions illustrating the versatility of this technique. A further advantage of the NAD route is that carrying out the polymerisation in a dispersion results in very effective removal of the acetic acid byproduct from the droplets as compared to diffusion of the acetic acid through a polymer

Table 4
Comparison of mechanical properties of melt and NAD prepared polymer

Method of preparation	IV	Flexural modulus (Gpa)	Tensile strength (Mpa)
Melt	0.6–0.8	10–12	120–140
NAD	1.25	12–13	220–260

melt. In addition to making it possible to carry out the polymerisation at temperatures below the melting point of the polymer, the polymerisations were significantly faster to reach a given molecular weight and no vacuum was required to reach high degrees of polymerisation i.e. the NAD process requires less complicated hardware compared with the traditional melt process.

5. Conclusions

Polymers based on poly(4-oxybenbenzoate-*co*-4-phenylene isophthalate) and poly(oxybenzoate-*co*-2,6-oxynaphenate) can be prepared by an NAD route in the presence of a hydrophobic organo-clay. The polymerisation unlike the melt polycondensation is not limited by the viscosity of the melt and high molecular weight and high melting to intractable polymers can be viably prepared by this process. Significant benefits are seen with respect to colour and mechanical properties. The hydrophobic organo-clay is believed to provide a steric barrier to coalescence thus preventing flocculation.

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