Preparation of submicrometre polyimide particles by precipitation from solution*

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The formation of submicrometre particles of high temperature polyimides by precipitation from a homogeneous solution in a mixed solvent of water and *N*-methyl pyrrolidone (H_2O/NMP) was investigated. The two polyimides consisted of those based on benzophenone tetracarboxylic dianhydride/2,2'-bis(4-aminophenyl)propane (BTDA-Bis A) and pyromellitic dianhydride/1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (PMDA-3F diamine). Phase diagrams of the BTDA-Bis A polyimide/NMP/H_2O ternary system were obtained for two solvent compositions through cloud point measurements. The observed mixed solvent composition dependence of the cloud point behaviour suggests that the water weight fraction plays a fundamental role in the solubility characteristics of polyimides. Preliminary precipitation studies indicate that the size distribution of the polyimide particles is governed by the cooling rate below the cloud point curve. At an average cooling rate of 23°C min^{-1}, narrow size distribution particles of 0.2 and 0.5 μm average diameter were obtained for the PMDA-3F diamine and the BDTA-Bis A polyimides, respectively. For slower cooling rates of 10 or 2°C min^{-1}, the particle size distributions were notably broader, probably as a result of nucleation and growth over a larger temperature range.

(Keywords: solution precipitation; polyimide particles; phase diagram)

INTRODUCTION

It is generally acknowledged that prepregs of carbon tows or cloths with high temperature polymers cannot be easily fabricated through melt prepregging processes because of intrinsically high melt viscosities and potential for thermo-oxidative degradation. However, recent studies indicate that prepregging processes based on the use of dried or dispersed polymer powders may present a solution to the challenging manufacture of high temperature polymer composites[1-3]. If such a strategy is to be adopted, the success in achieving appropriate fibre impregnation and prepreg consolidation, relies heavily on the ability to produce a stable colloidal dispersion of well defined, micrometre or even submicrometre polymer particles. The noted constraint on particle size is dictated by the need to achieve a specific distribution of resin particles between reinforcing fibres which should be on the average about 1–5 μm apart. (This number is calculated for a square array of AS4 carbon fibres (7–8 μm in diameter), using a volume fraction of reinforcing fibres, $v_f = 0.6$.)

A further point to be considered is the likely dependence of the glass transition temperature on particle size. As the size of a polymer particle decreases, the volume fraction of chains near the surface increases. The chains at the air/polymer interface have a larger free volume and might undergo a glass to liquid transition at a lower temperature than chains in the material bulk. Whether this prediction will hold in practice remains to be verified. Furthermore, the magnitude of the change in glass transition temperature with particle size, if observed, may or may not be significant. If it is significant, it is clear that it would greatly facilitate the consolidation step of composites manufactured by the dispersion prepregging process.

Several methods for the preparation of polymer particles, including emulsion polymerization[4], solution spraying[5], and polymer grinding[6] have been documented. Unfortunately, these extensively used methods are either non-applicable or unsuitable for the preparation of

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submicrometre particles of high temperature polyimides. The former method has only been utilized for polymers synthesized by chain growth polymerization processes. Solution spraying and grinding processes generally result in the formation of particles of average diameter in the range of 5–50 μm, depending on whether sonication was used prior to particle size analysis[5–7]. On the other hand, the precipitation method which has been previously used for the preparation of inorganic particles[8], may a priori offer a possible solution for the formation of fine particles of tough thermoplastic polymeric materials.

The principle behind the formation of polymer particles by precipitation from a polymer solution is certainly not novel. When an originally homogeneous polymer solution is brought across a binodal curve, phase separation will occur[9]. If the temperature and concentration for a polymer/solvent mixture are within the region encompassed by the binodal and spinodal curves in the phase diagram[10,11], phase separation takes place by a process of nucleation and growth. Such a process yields polymer-rich particles and a solvent-rich liquid phase. The average size and the size distribution of these particles are governed by their relative rates of nucleation and growth. In order to obtain very small particles of uniform size, one must maximize the nucleation rate and minimize the extent to which the particles are allowed to grow by coalescence. Even though particle nucleation theories have not yet been unambiguously tested with kinetic data of particle formation[12], it is of interest to examine the theoretical expression for the rate of homogeneous nucleation[13]:

$$N = N_0 \exp\left\{ -\left[\Delta G_d + \alpha \left(\frac{T_0}{\Delta T} \right)^2 \right] \Big/ kT \right\}$$

where N is the nucleation rate; N_0 and α are constants including respectively the frequency factor and the particle/liquid interfacial free energy; T_0 and T are respectively the binodal temperature and the temperature at which precipitation takes place; ΔT is the undercooling below the binodal curve (i.e. the difference between T_0 and T); ΔG_d is the activation energy for diffusion across the liquid–particle interface; k is the Boltzmann constant. If one wishes to obtain a narrow distribution of small particles, one must achieve a high rate of nucleation (i.e. precipitate the solution at relatively large undercooling ΔT). In other words, the time within which the temperature of the system is changed from T_0 to T must be as short as possible. To be certain that such conditions are met experimentally, one must know fairly accurately the phase diagram of the system under investigation.

In this research, the precipitation of two high temperature polyimides — pyromellitic dianhydride/1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane polyimide (PMDA-3F diamine polyimide) and 2,2′-bis(4-aminophenyl)propane/3,3′,4,4′-benzophenone tetracarboxylic dianhydride polyimide (BTDA-Bis A polyimide) — from a mixed solvent system of water/*n*-methyl pyrrolidone (H_2O/NMP) was studied. We will first describe the partial phase diagram for the polyimide/NMP/H_2O ternary system for two NMP-rich mixed solvent compositions. Then, conditions for particle formation and factors governing the formation of uniform, submicrometre particles will be discussed.

EXPERIMENTAL

Materials

The two polyimides studied were synthesized and characterized in our laboratories. BTDA-Bis A polyimide was end-capped with t-butyl phthalic anhydride. Its molecular weight was 20 000 g mol^{-1} as determined by end-group analysis by 400 MHz ^{1}H n.m.r. and its glass transition temperature, T_g, was 297°C. PMDA-3F diamine polyimide was end-capped with phthalic anhydride and had an intrinsic viscosity of 0.47 dl g^{-1} at 25°C in NMP, corresponding to a number average molecular weight of 18 500 g mol^{-1} as measured by ^{1}H n.m.r. A T_g of 422°C was measured by thermomechanical analysis at a rate of 10°C min^{-1} with a 10 g compressive force[14]. The chemical structures of these polyimides are shown in *Figure 1*. The NMP was dried over P_2O_5, distilled under vacuum and always used fresh. The non-solvent, water, was deionized prior to use and the polyimides were dried in a vacuum oven above their T_g prior to being dissolved.

Cloud point measurements

Cloud point curves were obtained for the BTDA-Bis A polyimide/NMP/H_2O system by light scattering

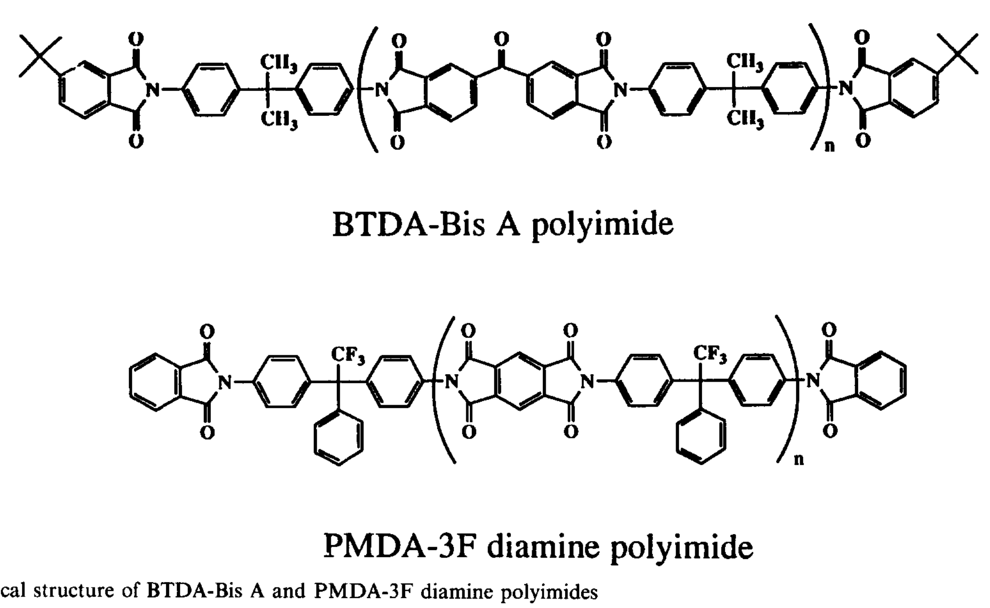

Figure 1 Chemical structure of BTDA-Bis A and PMDA-3F diamine polyimides

measurements at 90° scattering angle using a helium/neon laser as the light source and a photomultiplier tube as the scattered light intensity detector. For solutions of polyimide weight fraction ranging from 0.002 to 0.170 and H_2O/NMP compositions of 6/94 or 7/93 wt/wt ratios, cloud points were measured by cooling the solution from the homogeneous state at a rate of 2°C min^{-1} until a large increase in the scattered light intensity could be observed. The maximum temperature experienced by the polyimide solution was always less than 100°C to prevent hydrolytic degradation of the polyimide. When working with freshly distilled NMP and under sealed conditions, the cloud point temperature was highly reproducible to a precision of ± 0.5°C, suggesting that no chemical degradation took place during the measurement.

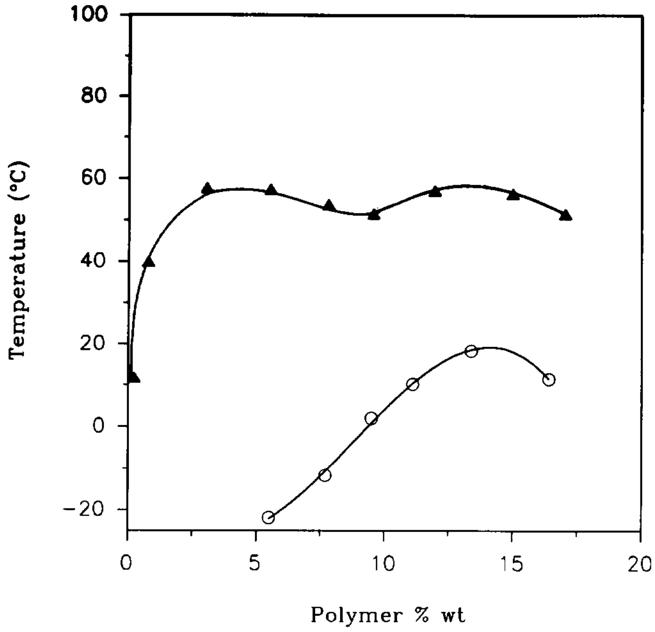

Figure 2 Cloud point curves for the BTDA-Bis A polyimide in the H_2O/NMP mixed solvent: ○, 6/94 H_2O/NMP; ▲, 7/93 H_2O/NMP

Polyimide particle preparation

Typical polyimide particles were prepared using the following conditions. The polyimide was added to a H_2O/NMP solvent mixture in a thermostatted metal cell equipped with a magnetic stirring bar and a thermocouple. The cell was air-tight, to ensure that the water content remained constant during the experiment. The sample cell was placed in a heating/cooling stage and heated up to a temperature at which an homogeneous solution was obtained (80°C and 90°C respectively for the 6% BDTA-Bis A and 4% PMDA-3F diamine polyimide solutions in 7/93 H_2O/NMP solvent mixtures). Then, the solution was cooled under constant stirring to 20°C at a certain cooling rate using a flow of cooled nitrogen gas. The cell was kept at 20°C for an additional 5 min before the particles were separated from the solvent-rich polymer solution. Examination of the phase behaviour (see Results and discussion section) showed that the BTDA-Bis A polyimide solution in equilibrium at room temperature with the swollen particles is very dilute in polyimide when the solvent mixture contains 7 wt% or more water. The dispersion of swollen polyimide particles was then spread on a glass slide and dried slowly in a vacuum oven at room temperature and studied in an ISI SX-40 scanning electron microscope (SEM) after gold sputtering. For more quantitative analysis of the particle size distribution, the dispersion was also dialysed in water for 5 days with a Spectra/por membrane (molecular weight cut off 1000 g mol^{-1}) obtained from Spectrum Medical Industries, Inc. The resulting particles were analysed in a Shimadzu SA-CP3 centrifugal particle size analyser. This apparatus measures particle sizes in the range 0.02–150 μm by determining optical density during particle sedimentation. The polyimide particles from the dialysis step were diluted with deionized water (18 MΩ resistivity) from a Nanopure II unit to obtain a suspension with initial turbidity in the range 60–140 units on the optical density scale of the instrument. All particle size measurements were run at room temperature, using a particle density of 1.4 g cm^{-3} (value determined for LaRC TPI™ by pycnometry).

RESULTS AND DISCUSSION

Cloud point curves for the BTDA-Bis A polyimide/NMP/H_2O ternary system are shown in *Figure 2* for water/NMP compositions of 6/94 and 7/93 wt/wt ratios, respectively. If the rate of cooling or heating was infinitely slow, the cloud point curve would correspond to the equilibrium phase boundary curve. Unfortunately, such slow experiments are not practical since these polymers are observed to crystallize very slowly from such solutions, as was observed in our polarized microscopy studies[15]. The cloud point measurement was thus designed to circumvent this problem. Examination of the cloud point curves surprisingly showed a very strong dependence of the phase diagrams on the water weight fraction in the mixed solvent. First, the maximum on the cloud point curve is raised by about 40°C when the water content in the mixed solvent is increased from 6 to 7 wt%. Second, while the cloud point curve exhibits a single maximum for the lower water content, it is characterized by two maxima at the higher water weight fraction. Although the results of a thorough study of the nature of these phase diagrams will be published separately[16,17], it suffices to say here that water plays a crucial role in the solubility characteristics of polyimides in mixed water/dipolar aprotic solvent systems. In such systems, ^1H n.m.r. studies carried out at various temperatures between 20 and 50°C suggest competitive hydrogen bonding processes among water molecules and between water protons and either NMP or polyimide carbonyl moieties[16,17]. Intrinsic viscosity investigations in mixed solvent systems (NMP/H_2O) indicate that at low concentration in the mixed solvent, water may act as a good solvent, whereas at higher concentrations, it will decrease the quality (increase the apparent χ) of the dipolar aprotic solvent for the polyimide. It should be noted that throughout these investigations, extreme care was taken to accurately determine the water weight fraction in the ternary systems. Furthermore, these observations emphasized the need to carry out the cloud point and precipitation studies in an environment sealed from the atmosphere, so as to avoid atmospheric water ingression in the ternary mixture during the experiment. These studies[16,17] also indicate that the intrinsic viscosity of a polyimide solution in NMP will vary by as much as 10% for an increase in water content in NMP from 0 to 3 wt%. It is thus clear that even small quantities of

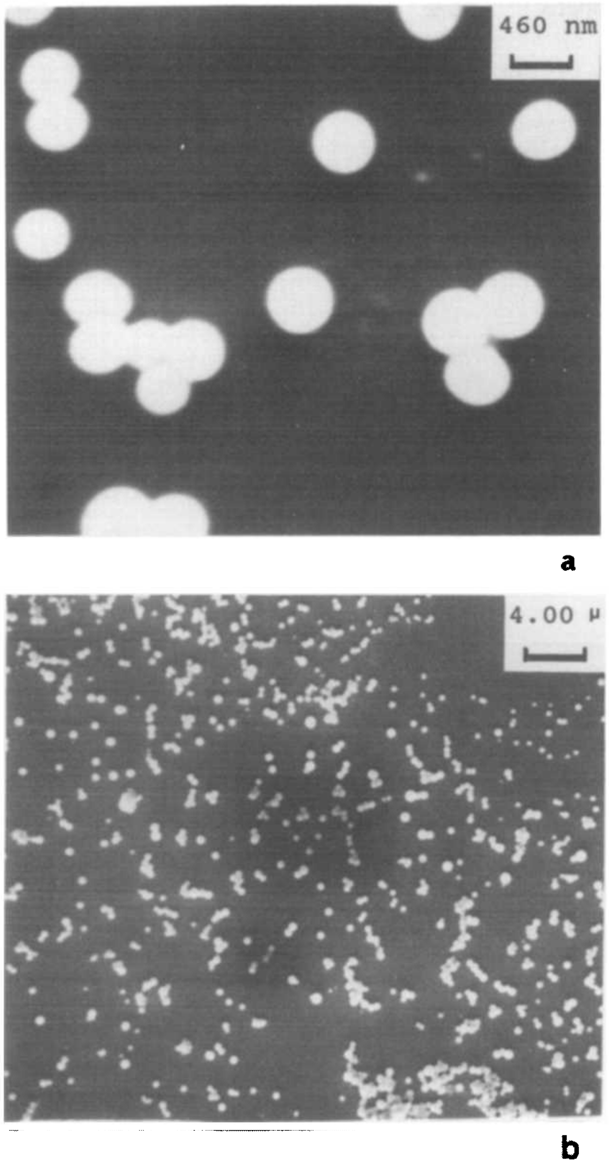

Figure 3 SEM photographs of BTDA-Bis A polyimide particles obtained by precipitation under a 23°C min^{-1} cooling rate; (a) and (b) correspond to different magnifications

water in NMP can change the hydrodynamic volume of polyimide chains in solution and that an accurate molecular weight determination of polyimides by gel permeation chromatography can only be achieved if the dipolar aprotic solvent used as the carrier phase is rigorously anhydrous.

To carry out the precipitation, one should, in principle, quench the homogeneous solution in the region between the binodal and the spinodal curves. In this study we have reported the cloud point curves for 6 and 7 wt% water content in the mixed solvent. However, since we do not yet know the location of the corresponding spinodals, we semi-arbitrarily chose a starting solution containing 6 wt% BTDA-Bis A polyimide and 94 wt% mixed solvent, where the solvent contains 7 wt% H_2O. This solvent composition was chosen on the basis that, ideally, it allows precipitation at room temperature under conditions where the maximum undercooling is sufficiently large (about 30–40°C) and where the resulting solvent-rich phase contains only a very small weight fraction of polyimide (about 0.002). The latter point is crucial when one desires to isolate the two phases produced by the precipitation process. Note that if we had selected a starting solution containing 6 wt% water in the mixed solvent, and carried out the quenching down to −20°C, the precipitation would have produced a solvent-rich phase containing a polyimide weight fraction of about 0.05 (i.e. 25 times richer in polyimide). In all cases, the quenching of the solution is never instantaneous, and, at the present time, we cannot claim that the precipitation carried out at the fastest cooling rate investigated took place in isothermal conditions. To investigate the temperature dependence of the precipitation process, the solution was cooled at rates ranging from 23°C min^{-1} down to 2°C min^{-1}.

Figure 3 shows the SEM photographs of particles prepared from the 6% BDTA-Bis A polyimide solution in 7/93 H_2O/NMP mixed solvent at a cooling rate of 23°C min^{-1}. Spherical particles of fairly narrow size distribution and an average diameter of 0.5 μm were obtained. The uniformity of the particles is demonstrated in *Figure 3b* and is further confirmed by the results obtained by quantitative particle size analysis (*Figure 4*). From the data shown in *Figure 4*, a median particle of 0.48 μm can be calculated, which compares very well with the value estimated from the SEM micrographs (*Figure 3*). The standard deviation about the median is 0.28 μm, which indicates a relatively narrow particle size distribution. The SEM photographs in *Figure 3* also suggest a low level of particle aggregation which is again confirmed by particle size analysis (see the small peak centred at 2–3 μm on the particle size histogram in *Figure 4*). When the precipitation was carried out at rates lower than 23°C min^{-1}, the particle size distribution was much broader. The SEM photographs in *Figures 5a* and *b* correspond to BDTA-Bis A polyimide particles precipitated from solutions of composition identical to those described earlier for cooling rates of 10°C min^{-1} and 2°C min^{-1}, respectively. It is clear then that the lower the cooling rate, the higher the temperature at which precipitation was initiated and the larger the temperature range where the particles were allowed to

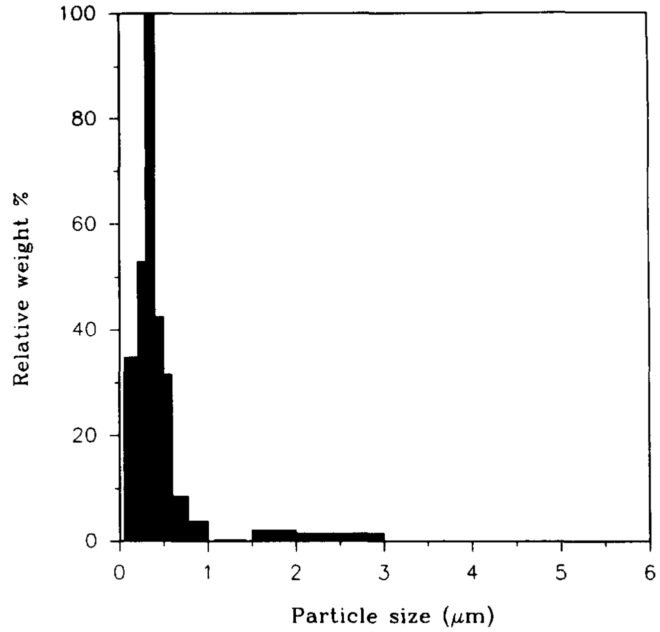

Figure 4 Size distribution of BTDA-Bis A polyimide particles obtained by particle size analysis

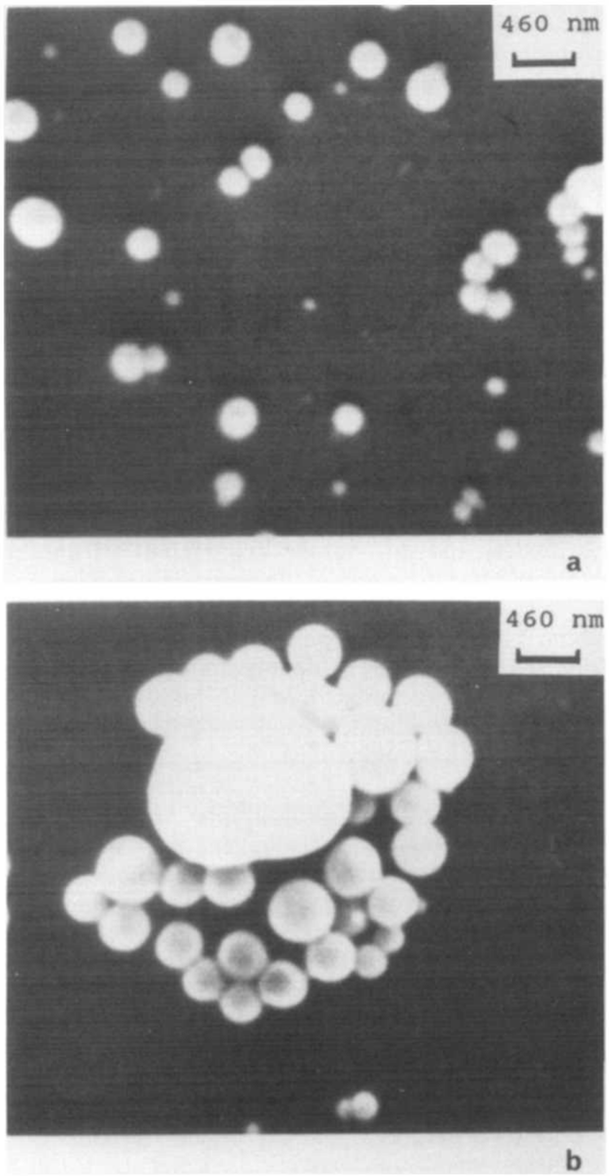

Figure 5 SEM photographs of BTDA-Bis A polyimide particles obtained by precipitation under cooling rates of (a) 10°C min^{-1} and (b) 2°C min^{-1}

nucleate and grow. In the absence of coalescence or aggregation of particles, correlations between particle size distribution and cooling rate are analogous to those encountered in the field of polymer crystallization[18]. Although we rationalize the effect of cooling on particle size and size distribution in terms of a nucleation theory, we cannot claim that the precipitation occurred only by a nucleation and growth process.

Last, we report preliminary results of the morphology of PMDA-3F diamine polyimide particles obtained by the same precipitation process. Further description of the room temperature ternary phase diagram of the PMDA-3F/NMP/H_2O system and a discussion of the effect of solvent, non-solvent and polyimide chemical structure on the nature of the phase diagram are provided elsewhere[16,17]. Because this polyimide has a T_g of 422°C and decomposes above 530°C, it may not be readily processable by melt techniques. It would therefore be an ideal candidate for prepregging from the powder dispersion state if small particles can be generated. Using the same light scattering technique, the cloud point temperature of a 4 wt% PMDA-3F diamine polyimide solution in a H_2O/NMP mixture containing 7 wt% H_2O was determined to be 51°C. Particles of this polyimide were formed by cooling a homogeneous solution from 90°C to room temperature at a rate of 23°C min^{-1}. *Figure 6* represents scanning electron micrographs of such particles at two different magnifications. Again, the particles are spherical and relatively uniform in size. A significant feature is that the average particle size is now about 0.2 μm. Whether this observation should only be accounted for by the lower initial polymer concentration in solution is not certain at this point. The role of other factors such as the polymer chain stiffness and thus the solution viscosity, the solvent/polymer interaction parameter and the effect of nucleating heterogeneities should also be investigated.

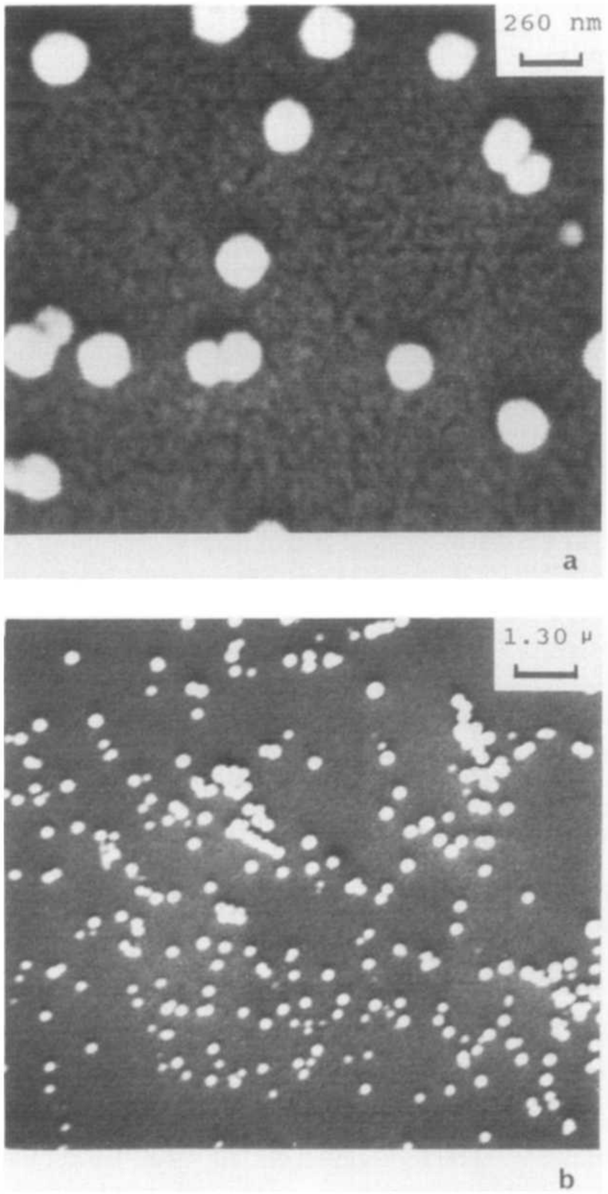

Figure 6 SEM photographs of PMDA-3F diamine polyimide particles obtained by precipitation under a 23°C min^{-1} cooling rate; (a) and (b) correspond to different magnifications

CONCLUSIONS

Uniform submicrometre particles of high temperature polyimides were prepared by a solution precipitation process. The particle size distribution is governed by the cooling rate through the cloud point curve where the system evolves from a homogeneous state to a final phase-separated (precipitated) state. The location of the cloud point curves and their shape is shown to be extremely dependent on the water concentration in the solution. Although the absolute magnitude of the average particle size may depend on the initial polymer concentration in solution, the shape of the coexistence curve and the quenching conditions in the two-phase region, our preliminary investigations indicate that for two polyimides of widely different chemical structures, the precipitation process, when properly controlled, leads to the formation of submicrometre particles.

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