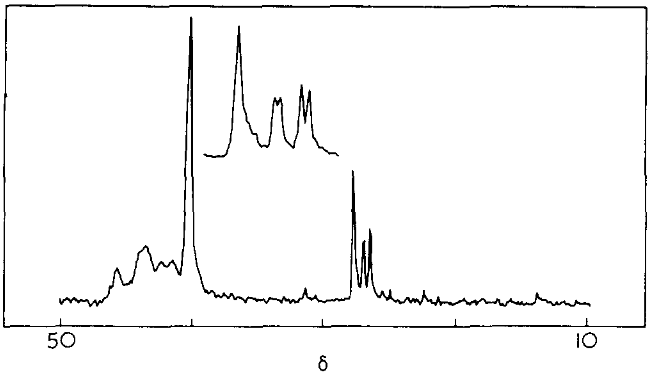

Figure 2 10–50 δ plot of the ^{13}C-n.m.r. spectrum for polystyrene with ^{13}C-labelled end-groups. An expansion of the methyl resonances is inset

Figures 1A and *1B* but prepared with AIBN containing carbon-13 only at its natural abundance, is displayed in *Figure 1C*. The peaks at *ca.* 25.55δ and *ca.* 30.15δ (*Figures 1A* and *1B*) correspond to methyl groups in initiator fragments, $(CH_3)_2C(CN)$, combined in the polymer. The peak at *ca.* 25.05δ (*Figure 1A* arises from occluded initiator which is almost completely removed by reprecipitation. Polymer recovered from the reaction mixture by precipitation in methanol shows the peaks corresponding to the end-groups but the peak associated with the initiator itself was not prominent showing that occlusion of initiator was less important under these conditions. Tetramethylsuccinodinitrile (TMSDN), formed when AIBN is decomposed in benzene or other inert solvent, gives rise to a methyl resonance at 23.25δ; it is evident from *Figure 1A* that very little TMSDN is occluded even in polymer precipitated only once in hexane.

Figure 2 shows the ^{13}C-n.m.r. spectrum of polystyrene prepared with ^{13}C-AIBN, precipitated in hexane and subsequently reprecipitated in the same liquid. The peaks at 26.5–27.15δ arise from combined initiator fragments; as in the case of polyMMA, the amount of occluded initiator in the purified polymer is small.

Figures 1B and *2* show clearly that the initiator fragments combined in polyMMA or in polystyrene give rise to methyl resonances with chemical shifts dependent on the nature of the adjacent monomer unit; the peaks show fine structure. It is evident that the use of initiator enriched in carbon-13 can lead to information concerning the units at or near the ends of polymer or copolymer chains and therefore on the reactions occurring early in the growth of a macromolecular chain. Studies of this type will be reported in subsequent publications.

The work described here was performed while N.W.E.H. held a Research Studentship awarded by S.E.R.C.

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Polymer–filler interactions in composites with grafted filler particles

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PMMA grafts were grown from the surfaces of glass beads and the grafted beads were used to fill PMMA homopolymer using solvent casting procedures. Interactions between grafts and matrix chains were investigated by examination of scanning electron micrographs of fracture surfaces of composite materials. It was demonstrated that, while grafts on adjacent beads are mutually miscible, grafts are immiscible with homopolymer chains at equilibrium. Formation of entanglements between graft and homopolymer chains was achieved by forming homopolymer *in situ* and avoiding equilibrium conditions.

Key words Poly(methyl methacrylate) entanglements; filler; grafts; homopolymer; interface; miscibility

Introduction

Following our development of a technique for growing polymeric grafts from glass surfaces[1], we attempted to use the procedure to modify interfaces in, and the mechanical properties of, glass-filled polymers. In our preliminary experiments chains of polystyrene (PSt) and of poly(methyl methacrylate) (PMMA) were grown from the surfaces of glass beads. Any homopolymer formed concurrently was removed by washing with a suitable solvent. The presence of grafted chains was confirmed by pyrolysis, by infra-red spectroscopy and by the fact that grafted beads adhered to each other strongly, after removal of solvent, as described previously[1].

Samples of grafted beads were mixed with the corresponding homopolymer (to 10% w/w) in a small extruder, the extrudate was fragmented and compression-moulded into plaques (3 mm thick). Standard dumbell-shaped specimens were cut from the plaques using suitable jigs and the sample surfaces were polished to remove surface defects. The tensile properties of such test pieces were compared with those of samples filled with ungrafted beads and prepared under identical conditions. According to these studies the properties of polymers filled with grafted and with ungrafted beads were virtually identical[2]. That is, no evidence was obtained for a modified filler-matrix interface in the presence of grafted beads.

We were concerned that the results of these preliminary experiments were unrealistic in that inherently favourable entanglements between the graft and matrix chains may not have developed under the conditions of these

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experiments. Lack of interaction could have arisen, for example, because of scission of the grafts from the beads during mixing and extrusion or due to incomplete mixing of the chains on the time scale of our procedures (we found it almost impossible to achieve a uniform distribution of beads in the polymer matrices). We therefore endeavoured to re-examine the situation using milder but more favourable conditions for sample preparation and in this communication we report on a study of fracture surfaces of such composites containing glass beads with grafted chains.

Experimental

Essentially the same procedure as described previously[1] was used to attach trichloroacetyl groups to the surfaces of soda-lime beads (Potters–Ballotini Ltd.), average diameter 30 μm; namely, surface hydroxyl groups were replaced by chlorine and then by phenyl groups which were subsequently acylated with trichloroacetyl chloride. In this work additional precautions were taken to ensure clean reaction conditions. After removing magnetic particles from the crude beads with a strong magnet, traces of iron were removed by washing with concentrated hydrochloric acid until tests for Fe(III) with potassium thiocyanate were negative; the beads were then refluxed with propan-2-ol. Also, greater precautions were taken during the phenylation stage (using lithium phenyl) to prevent the ingress of air.

Molybdenum hexacarbonyl (80 C) was used to generate radicals from the trichloroacetyl groups and, hence, to initiate graft polymerization of methyl methacrylate (MMA)[3]; polymerization reactions were performed under vacuum and reactions were taken to high conversions of molybdenum carbonyl. Some PMMA homopolymer was formed during graft polymerization and this was removed by washing with ethyl acetate. The amount of grafted polymer attached to the beads was determined by pyrolysis.

PMMA homopolymer used to form composites with grafted beads was a standard polymer (PMMA2, $\bar{M}_n$ =48K) supplied by RAPRA.

Fracture surfaces of various samples of composites containing grafted beads were examined using a Cambridge Mk. III scanning electron microscope.

Results and Discussion

Samples of grafted beads used in this study contained 0.5–3.0% (w/w) PMMA grafts, determined after washing several times with solvent; the results obtained were independent of polymer content within these limits.

Figure 1 shows a scanning electron micrograph of the fracture surface of a sample of washed beads (1.67% (w/w) PMMA; equivalent to a layer 0.180 μm thick on beads 30 μm diameter) after removal of solvent. This micrograph is very similar to one published previously[1] and shows a collection of essentially smooth beads in which adhesion between them is apparent at their points of contact. This adhesion must arise from entanglements between grafted chains. Blemishes on the surfaces of the beads are fracture surfaces formed by breaking some beads from the remainder of the material.

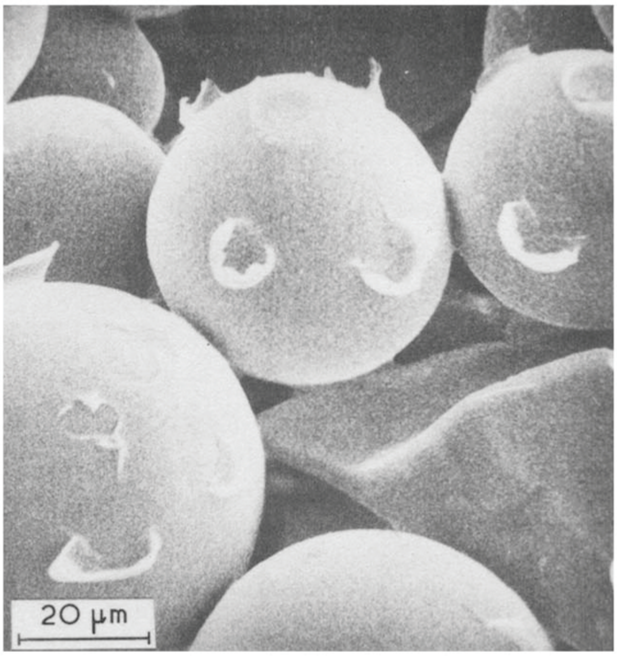

Figure 1 Fracture surface of PMMA-grafted glass beads after washing to remove all soluble polymer and drying

Samples of grafted, washed beads, such as that depicted in *Figure 1*, were readily dispersed in solvents for PMMA, e.g. in ethyl acetate or toluene. Solvents penetrate the layer of graft polymer and destroy the interparticle adhesion. In the presence of solvent, grafted beads could be stirred freely but on removal of solvent they again formed a hard reticulated mass. Therefore entanglements between grafted chains on different beads can be repeatedly destroyed and formed by addition and removal of solvent. In other words, in the presence of solvent there is no barrier to the rapid formation of entanglements between grafted chains as the local volume fraction of polymer increases on solvent removal.

PMMA homopolymer was added to grafted, washed beads and sufficient toluene was added to dissolve the polymer and render the whole system mobile. The samples were thoroughly mixed and solvent was removed by evaporation and subsequent heat treatment under vacuum. Samples were prepared as thin films in flat-bottomed petri dishes. During solvent removal the dense beads settled to the bottom in mobile systems. To maintain a dispersion of beads the samples were inverted from time to time. Even so, a uniform distribution of beads in homopolymer was not achieved. In some cases hompolymer filled the voids between beads and maintained a separation of the beads. In other cases homopolymer did not fill the voids.

Figures 2 and *3* show a series of scanning electron micrographs of composites formed from PMMA-grafted beads and PMMA homopolymer.

Figure 2 consists of three scanning electron micrographs of fracture surfaces of a sample prepared by mixing grafted beads and PMMA in toluene for 24 h at room temperature, then slowly removing solvent to produce a film which was subsequently heated under vacuum for one hour at 200 C to remove the remaining solvent. *Figure 3* is a corresponding micrograph of a sample prepared by mixing as before, removing the bulk of the solvent at room temperature over a period of twelve hours and gradually increasing the temperature to 80°C to remove residual solvent.

The distinctive feature of these micrographs is the lack of evidence for any form of interaction between the beads

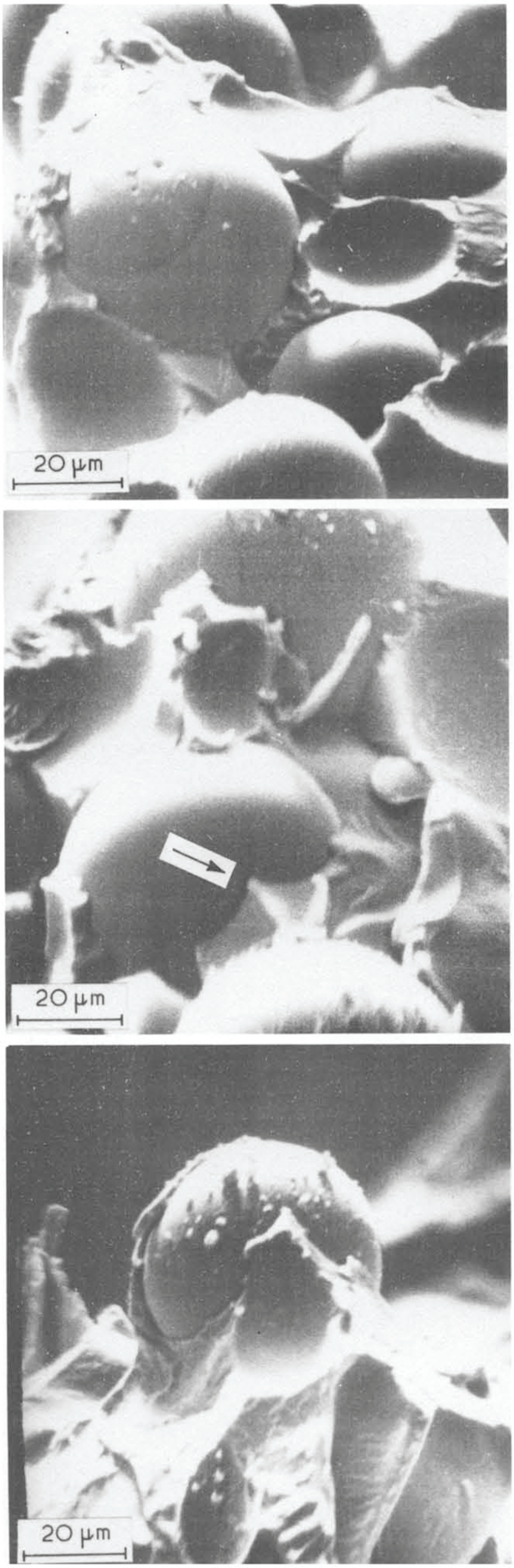

Figure 2 Scanning electron micrographs of fracture surfaces of PMMA-grafted glass beads after solution casting with PMMA homopolymer and annealing at 200°C under vacuum

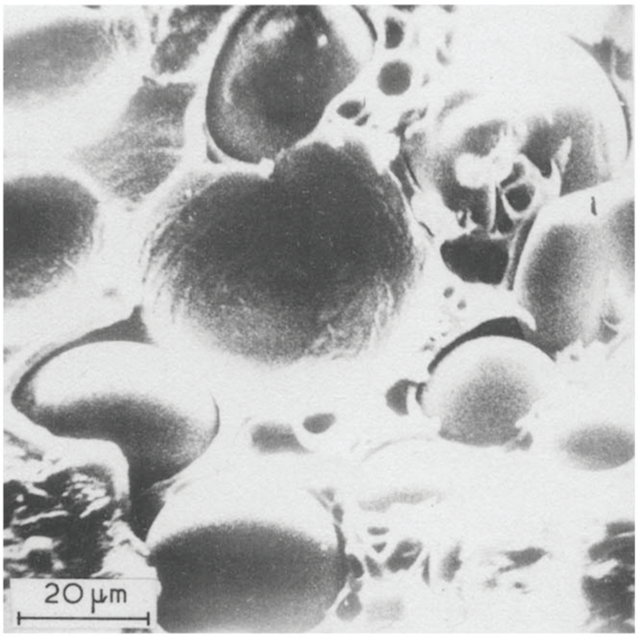

Figure 3 Scanning electron micrograph of fracture surface of PMMA-grafted beads after solution casting with PMMA homopolymer and heating at 90°C under vacuum

and the matrix involving entanglements between grafted and homopolymer chains. Fracture occurs at a polymer–polymer interface and not at a polymer–glass interface. In the main, beads at the fracture surface and regions of the matrix where beads have been removed on fracture exhibit smooth surfaces. In *Figure 3* there appear to be definite voids between the matrix and the grafted beads.

These observations may be compared with, for example, those of Wambach *et al.* who studied fracture surfaces of poly(phenylene oxide) (PPO)[4]. Their micrographs of PPO filled with untreated beads, showing generally smooth surfaces of beads and matrix with no interaction between them, are similar to our micrographs of PMMA filled with grafted beads as illustrated in *Figures 2* and *3*. In contrast, micrographs published by Wambach *et al.* using silane treated beads show definite evidence of interactions between the matrix and the beads, the interfaces are characterized by many polymer fibrils extending from the matrix to the beads. Our micrographs show only occasional features, e.g. arrowed in *Figure 2b*, which could possibly be construed as indicating good adhesion between the matrix and grafted beads.

On mixing grafted beads and homopolymer in the presence of solvent it appears that, even if graft and homopolymer chains entangle in the presence of solvent, as solvent is removed the homopolymer and graft chains separate. That is, the system behaves as if graft and homopolymer chains are immiscible in bulk and effectively undergo phase separation as solvent is removed. Thus, the solution of homopolymer and grafted beads forms two phases as solvent is removed and, as the homopolymer phase decreases in volume, the matrix contracts away from the beads, effectively leaving the beads in voids and unattached to the matrix, as seen in *Figure 3*. When samples are subsequently heated to 200°C, i.e. well above the glass-transition temperature of PMMA, the whole sample anneals and the voids disappear. There then appears to be close contact between the beads and the matrix, *Figure 2*, but no mixing of graft and free polymer chains.

Even when bound and free polymer chains are inherently immiscible, miscibility and consequent interactions may be achieved if equilibrium conditions can be avoided. This situation is often encountered in blends of block copolymer with homopolymer. We have obtained evidence for such interactions between matrix and graft chains in this work by operating under conditions specially chosen to avoid equilibrium.

A sample of functionalized glass beads were heated at 80°C for $2\frac{1}{2}$ h in the presence of an equal volume of MMA containing molybdenum hexacarbonyl (1.5×10^{-3} mol l^{-1}). These conditions gave extensive formation of PMMA homopolymer. Instead of isolating the grafted beads from the reaction mixture the reaction vessel was opened and all residual monomer was removed by evaporation under vacuum. The product was a hard ceramic-like material, containing 9.5% (w/w) PMMA, in the shape of the reaction vessel; subsequent washing and pyrolysis established that the beads carried 1.6% (w/w) PMMA as grafts. *Figure 4a* is a low-magnification scanning electron micrograph of the sample which clearly shows the porous nature of the material and the presence of polymer on the surfaces of the beads. Closer examination of the fracture surfaces, *Figures 4b* and *c*, demonstrates the separation of a polymer layer from the beads and shows evidence, in the form of polymer fibrils, for adhesion between that polymer layer and the surfaces of the beads. Undoubtedly fracture causes separation of the homopolymer layer from the graft polymer; the fibrils are a consequence of entanglements between the two types of polymer chain.

In this latter situation equilibrium conditions were intentionally avoided by forming PMMA homopolymer *in situ* in a highly viscous system. The overall conversion of MMA to PMMA was 30%. During polymerization unreacted MMA acts as solvent for homopolymer and grafts. As the PMMA content increases, corresponding to situations encountered during preparation of composites of grafted beads and homopolymer, separation of homopolymer and grafts may occur. However, the grafts would still be swollen with monomer from which further homopolymer would form and the local viscosity in the system would eventually become so great that homopolymer would be unable to diffuse from the grafts on the time scale of the experiments. Thus, entanglements between graft and homopolymer chains would arise from not establishing equilibrium conditions. This situation is closely analogous to that which we discussed previously[5] for blends of block/graft copolymers with one homopolymer where phase separation occurs if sufficient time is allowed for equilibrium to be achieved but can be avoided by casting the mixture from homogeneous solution on a time scame such that viscosity effects restrict equilibration.

On the basis of the above observations we conclude

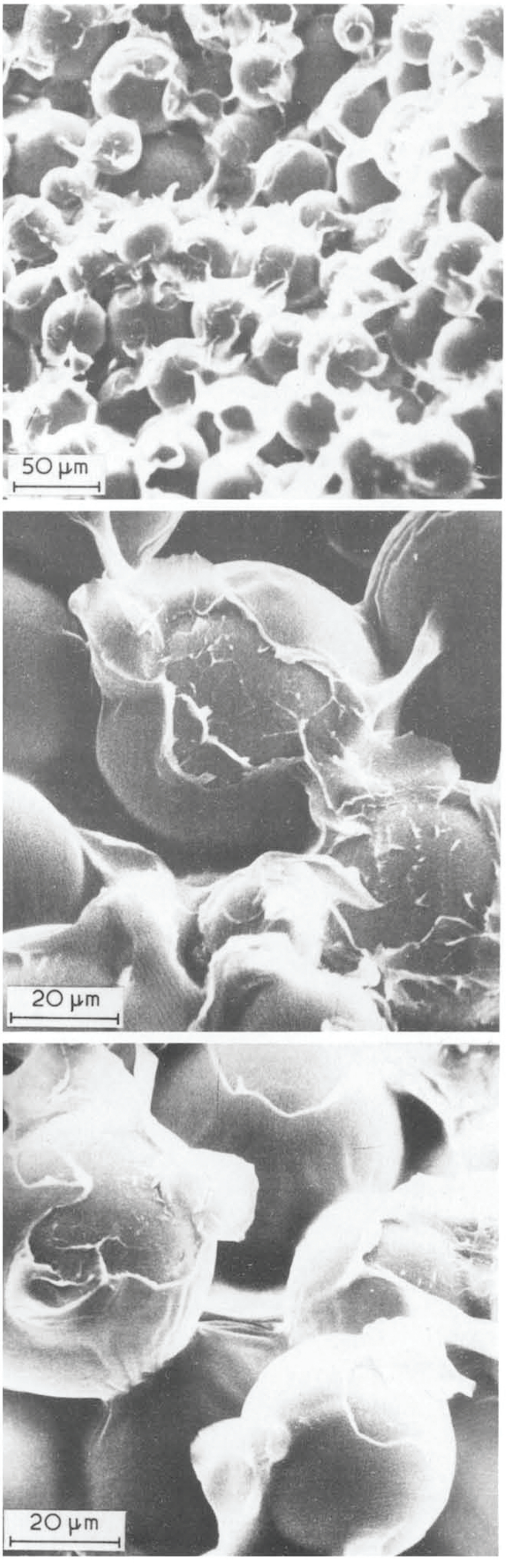

Figure 4 Fracture surfaces of PMMA-grafted glass beads as formed on polymerization after removal of volatiles but without removal of soluble PMMA-homopolymer

that graft chains bound to the surface of one bead are miscible with similar bound chains on another bead but not with free homopolymer chains. This conclusion is not really surprising in view of our previous report that block/graft copolymers are, to a first approximation immiscible with homopolymer[5], i.e. chains of homopolymer and the corresponding blocks in copolymers do not mix at equilibrium. It should make no real difference in determining the miscibility of free homopolymer and bound chains whether the bound chains are grafts attached to glass beads or blocks attached to a domain or microphase of different polymer in a block or graft copolymer. This study therefore extends the range of systems which demonstrate immiscibility of free and bound polymer chains which must arise from an unfavourable entropy of mixing because mixing chemically identical grafts and homopolymer chains should be athermal. The only factors which should be important in determining the miscibility of bound and free chains should be the number of chains per unit area of impenetrable interface, the molecular weights of the chains and whether or not equilibrium is achieved. To obtain a detailed understanding of this situation we need to be able to determine and vary the density and lengths of bound chains. We have recently developed a technique for detachinggrafts from glass beads and isolating them for characterization[6]; we hope to describe the procedure in a separate publication. Present indications are that the molecular weights of the grafts on the surfaces of the beads have a hibher molecular weight than the homopolymer used in forming the composites; a situation which should favour miscibility[7].

The conclusion that free and bound polymer chains are generally immiscible has important implications with respect to the nature and properties of many composite materials. Physical separation of bound and free chains to form weak polymer–polymer interfaces could result in composites with inferior properties to those in which the surface of the dispersed phase was treated in some way to produce a favourable interaction between the matrix and the dispersed phase. Alternatively, composites with potentially good properties could be prepared by choosing situations which avoid the equilibrium separation of bound and free chains, as illustrated in this study, or by chemically attaching the bound and matrix chains, e.g. by crosslinking.

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High molecular weight polyesters from alkali metal dicarboxylates and α,ω-dibromo compounds

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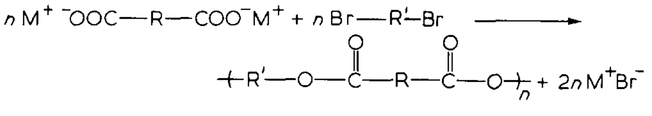
The reaction of alkali metal salts of dicarboxylic acids with α,ω dibromo compounds to form high molecular weight polyesters is best performed using the caesium salts of the acids in *N*-methyl pyrrolidone.

Key words Polyesters; condensation; dicarboxylates; alkyl dibromides; fibre-forming

Introduction

There are several references[1-4] in the literature to the synthesis of polyesters *via* the reaction:



$$n\,M^+\,{}^-OOC{-}R{-}COO^-M^+ + n\,Br{-}R'{-}Br \longrightarrow {\left[R'{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O\right]}_n + 2n\,M^+Br^-$$

However, as far as we are aware, the procedures described give rise only to relatively low molecular weight products. Recently, there have been attempts to apply phase transfer catalysis to this reaction[5-7]; here again, yields were far from quantitative and molecular weights were relatively low. We wish to report results which define the conditions under which the above reaction leads to a high molecular weight polymer. Whilst most of the study has been devoted to the preparation of poly(decamethylene terephthalate) (10 GT), preliminary observations suggest that the procedure is of general application. With the appropriate choice of solvent, counterion and temperature, the reaction to form polyesters can be rapid, virtually quantitative and gives rise to fibre forming polymers with number average molecular weights in excess of 10 000.

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