

Conclusions

We believe we have obtained clear evidence that amorphous material can be prepared from solution by drastically quenching the polyaryls PEEK and PEK. In each case the amorphous material has a distinctive bead-like morphology; it can be crystallized by annealing, and on crystallization it adopts the usual crystal structure of the polymer. The appearance of two phases on quenching is consistent with liquid-liquid phase separation. This may arise as the system is quenched, rapidly, into a biphasic region at high supercooling. We are able to reach this biphasic region because the rigid nature of the molecules only permits slow crystallization rates and hence we can quench into the biphasic region before significant crystallization occurs. Furthermore, because the glass transition temperatures, T_g , of pure PEEK and pure PEK are particularly high at 144 and 154°C, respectively⁷, solutions of the polymers, especially in high melting point solvents such as benzophenone ($T_m \approx 48^\circ\text{C}$), will also have high values of T_g . Therefore, under conditions of rapid quenching, one (or both) of the phases may be cooled below its T_g very quickly without allowing sufficient time for crystallization of the polymer, thus leading to an amorphous precipitate.

Further work (to be published) explores the phase diagram and supports the suggestion that where two morphologies are found in the same preparation one

vitrifies from the polymer-rich, and one crystallizes from the polymer-poor phase. Similar behaviour has previously been found by Arnauts and Berghmans⁸ and Hikmet *et al.*⁹ with atactic polystyrene solutions although in these cases both polymer-rich and polymer-poor phases produce amorphous polymer but, as shown in reference 9, in a distinctly two-component morphology.

There is clearly scope for much further work on these systems, but we feel that the main effect – the production of amorphous polyaryl entities from dilute solution – is clearly established.

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Preparation of polystyrene with tertiary amine end groups and its use in block copolymerization by a photoinduced process

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A new azo-initiator has been synthesized which facilitates the preparation of polymers with tertiary amine end groups. Subsequently, polystyrene obtained by this way was used in photoinitiation of polymerization of methyl methacrylate in the presence of 9-fluorenone.

(Keywords: azo-initiator; photoinitiation; block copolymer)

Introduction

Light induced synthesis of block and graft copolymers has several advantages over other methods^{1,2}. Selective and efficient formation of block and graft copolymers may be accomplished by u.v. irradiation of appropriate amine-containing prepolymers in the presence of aromatic ketones and vinyl monomers. Kinstle and Watson³ prepared poly(styrene-co-*N,N*-dimethylamino-styrene) from polystyrene. Irradiation of this polymer and benzophenone with u.v. light in the presence of 2-ethylhexylmethacrylate yielded predominantly graft copolymer. Ledwith⁴ outlined a potential synthetic route of 9-fluorenone-tertiary amine combination for the synthesis block and graft copolymers.

Recently, we have been investigating⁵⁻⁸ the possibility of preparing block copolymers utilizing azo-initiators. Such materials are of considerable interest as thermal and photochemical initiators. Attachment of functional groups to polymers as terminal units may easily be achieved⁹ using these initiators.

This note reports the synthesis of a new free radical azo-initiator and its use for the preparation of tertiary amine terminated prepolymers. In addition, polystyrene obtained by this method was used in conjunction with 9-fluorenone in a photo-redox system for free radical polymerization of methyl methacrylate (MMA).

Experimental

Materials. Solvents and monomers were purified according to the conventional drying and distillation procedures. 4,4'-azobis(4-cyanopentanoic acid) (Fluka, Switzerland) was used without further purification. 9-fluorenone (BDH, UK) was recrystallized from ethanol, m.p. 82.5–83.5°C. *N,N*-dimethyl ethanol amine (Fluka) was refluxed for several hours and fractionally distilled; the middle fraction was collected.

Synthesis of 4,4'-azobis(*N,N*-dimethyl amino ethyl-4-cyanopentanoate) (ADCP). A solution of 2.5 g of 4,4'-azobis(4-cyanopentanoic acid) (ACPC), which