polymer communications

Carbon-13 n.m.r. study of end-groups in polymers prepared using azoisobutyronitrile as radical initiator

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^{13}C-azoisobutyronitrile has been used to initiate polymerizations of methyl methacrylate and styrene The n.m.r. spectra of the resulting polymers show peaks arising from the combined initiator fragments with chemical shifts dependent on the nature of the adjacent monomer unit

Key words Polymerization; ^{13}C-nuclear magnetic resonance; end-groups; styrene; methyl methacrylate, azoisobutyronitrile

Rates and efficiencies of initiation in radical polymerizations involving azoisobutyronitrile (AIBN) have been determined from the results of end-group analyses of the resulting polymers, using ^{14}C-initiator to achieve the required sensitivity and accuracy[1]. The efficiencies found for esters of methacrylic acid are generally much less than that for styrene[2]. Various possible explanations for this difference are being tested; as part of the programme, ^{13}C-n.m.r. specroscopy is being applied to the study of the end-groups derived from AIBN, using initiator enriched in its methyl groups with carbon-13. The results of the first experiments are now reported.

Polymers of methyl methacrylate (MMA) and styrene were prepared at low conversions in benzene solution at 60°C in vacuum dilatometers using ^{13}C-AIBN as initiator. Polymers were precipitated from the reaction mixtures using either hexane or methanol; in some cases, they were further purified by reprecipitation from solutions in benzene. All materials had been purified by standard procedures. The initiator had been prepared using 0.5 g methyl-labelled 1,3-^{13}C-acetone (90 atom %) supplied by B.O.C. Ltd.; the labelled acetone was diluted so that, in the final product, the isotopic abundance of carbon-13 in the methyl groups was approximately 20%.

Carbon-13 n.m.r. spectra were determined at ambient temperature using a JEOL FX 100 Fourier-transform spectrometer operating at 25.05 MHz. Samples (70–100 mg) were dissolved in $CDCl_3$ (2.2 ml) and the solutions were filtered. Spectra, 500 Hz (200 p.p.m.) in width, were accumulated into 8K (8192) data points and zero filled to 16K data points before Fourier-transformation using an exponential weighting function introducing 0.7 Hz line-broadening. The pulse repetition time was 1.0 s using a tip angle of 54°. Chemical shifts, quoted to the nearest 0.05 p.p.m., were referenced *via* the central $CDCl_3$ solvent resonance at 76.9δ.

Figure 1A shows the ^{13}C-n.m.r. spectrum of a sample of polyMMA prepared using ^{13}C-AIBN and precipitated in hexane but not reprecipitated. *Figure 1B* refers to the same polymer after reprecipitation in hexane. The spectrum of another sample of polyMMA, similar to that referred to in

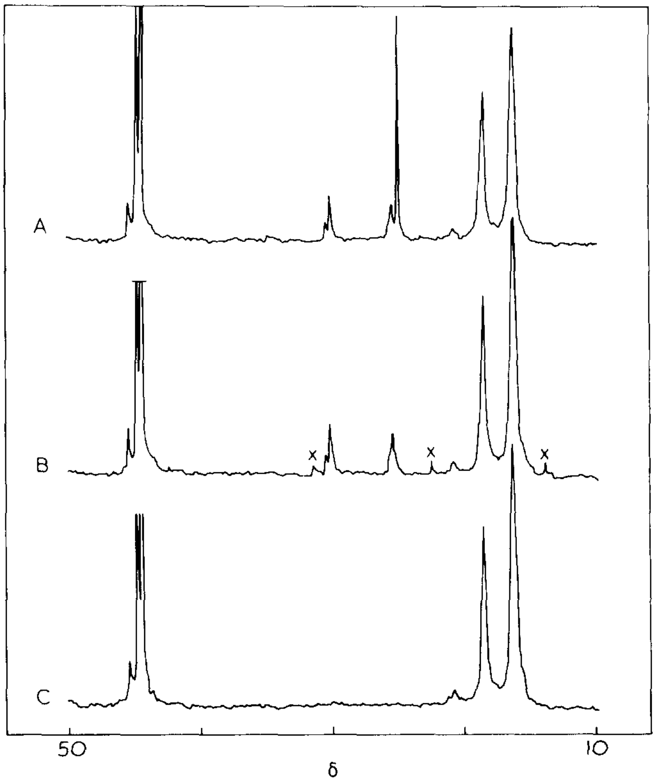

Figure 1 10–50 δ portions of ^{13}C-n.m.r. spectra for (A) polyMMA with ^{13}C-labelled end-groups, precipitated once in hexane; (B) as (A) but precipitated twice in hexane; (C) unlabelled polyMMA. The group of resonances at *ca.* 45 δ has been allowed to go off-scale. Signals marked x are due to residual hexane

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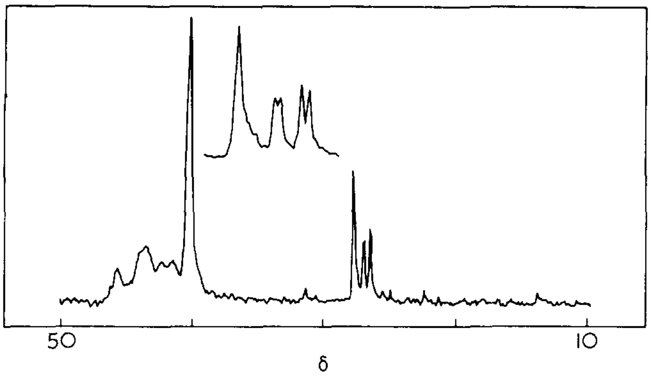

Figure 2 10–50 δ plot of the ^{13}C-n.m.r. spectrum for polystyrene with ^{13}C-labelled end-groups. An expansion of the methyl resonances is inset

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.

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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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