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Preparation of Block Copolymers of Styrene and 2-Methyl-2-Oxazoline

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Introduction

Iodine has been reported to initiate the polymerisation of styrene (TRIFAN and BARTLETT 1954; KANOH et al. 1962) and the resulting polystyrene was found to contain more than 10% of iodine. It was suggested that the iodine was largely present as $ICH_2CH(C_6H_5)\sim\sim$, and to a lesser extent, as $\sim\sim CH_2CH(C_6H_5)I$. These terminal entities, being alkyl iodides, ought to be capable of initiating the polymerisation of 2-oxazolines (SAEGUSA et al. 1972) thereby providing a method for the synthesis of block copolymers of styrene and 2-oxazoline. Two such copolymers have now been prepared by this route.

Experimental

Polystyrene. The polymerisation reactor was a 50 ml flask to which were attached two ampoules fitted with breakseals. In one ampoule there was 5 ml of styrene purified by distillation from dibutylmagnesium and in the other 0.51 g of doubly sublimed iodine. The flask was evacuated and 5 ml of 1,2-dichloroethane was distilled under high vacuum and the flask was sealed with a flame. The breakseals were ruptured and the resulting mixture was stored at 20°C in complete darkness for 18 days. The vessel was then opened and 2 ml methanol added to terminate polymerisation. The contents were dissolved in 100 ml chloroform, shaken with aqueous sodium thiosulphate, washed with water and dried over calcium hydride. On removal of the solvents and unreacted styrene monomer on a rotary evaporator, polystyrene (5g) was obtained as a colourless gum.

Styrene-oxazoline copolymer. A solution of 3.79 g of the polystyrene and 4.76 g 2-methyl-2-oxazoline in 20 ml of freshly distilled dimethylformamide was refluxed for 36 hours under nitrogen. Solvent and unreacted oxazoline were then removed on a rotary evaporator at 100°C, leaving an involatile viscous yellow liquid. This was dissolved in 5 ml of chloroform and precipitated with carbon tetrachloride, then three times in succession from its chloroform solution by diethyl ether. (Analysis of the CCl_4 and ether solutions by NMR and IR showed that the solute was mainly polystyrene, and these were accordingly not studied further.) The yellow solid thereby obtained was dried

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under vacuum, then 50 ml of methanol was added. The insoluble fraction was collected by centrifugation, washed with methanol and dried under vacuum to yield 0.16 g of a yellow powder, designated copolymer fraction 1. The methanol solution was evaporated to small bulk and the solute was precipitated from it by diethyl ether as a yellow solid. After washing with ether and drying under vacuum the yield of powder, designated copolymer fraction 2, was 3.64 g.

The solubility characteristics of the copolymer fractions 1 and 2 are summarised in Table 1, together with those of the precursor polystyrene.

TABLE 1

Solubility of homo- and block-copolymers of styrene and 2-methyl-2-oxazoline

Solvent	Polystyrene	Poly (2-Me-Ox)	Copolymer fraction 1	Copolymer fraction 2
H_2O	I	S	I	I
CH_3OH	I	S	I	S
C_2H_5OH	I	S	I	S
$(C_2H_5)_2O$	S	I	I	I
THF	S	I	I	I
$CHCl_3$	S	S	S	S

I - insoluble S - soluble

In the IR spectrum of copolymer fraction 1 (Figure 1), the absorption band at 1630 cm^{-1} is assigned to the c=o stretching mode of the tertiary amide unit and the absorption at 700 cm^{-1} to the C-H bending vibrations of the aromatic ring.

The NMR spectrum of copolymer fraction 1 (Figure 2) shows six broad signals centred at 1.46 δ ($-C-CH_2-C$), 1.83 δ (CH-Ar), 2.10 δ (CH_3-CO-N), 3.45 δ ($-CH_2-N$) and aromatic protons at 6.55 and 7.08 δ. (The signal at 5.32 δ is due to residual protons in the incompletely deuterated solvent.)

These spectral data show the presence of both styrene and 2-methyl-2-oxazoline moieties in copolymer fraction 1. The IR and NMR spectra of copolymer fraction 2 show features similar to those seen in Figures 1 and 2. Integration of the signals at 3.45, 6.55 and 7.08 δ showed that copolymer fractions 1 and 2 respectively contained 66 and 83 mol % methyl oxazoline residues.

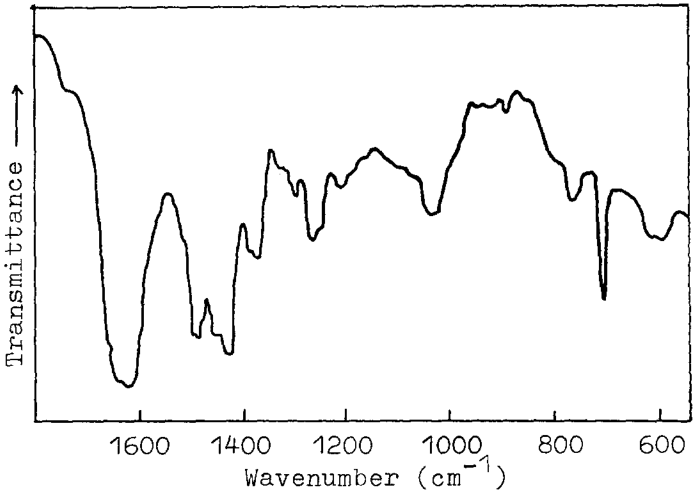

FIGURE 1. IR spectrum of copolymer fraction 1 (KBr disc)

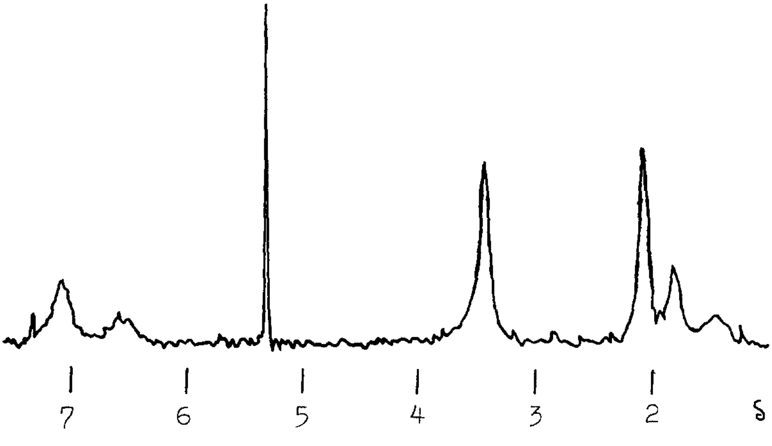

FIGURE 2. NMR spectrum of copolymer fraction 1 in CD_2Cl_2

It can be seen from Table 1 that the non-polar solvent diethyl ether is a solvent for polystyrene but a non-solvent for copolymer fractions 1 and 2. The polar alcohols are non-solvents for polystyrene, but do dissolve copolymer fraction 2: that copolymer fraction 1 is insoluble is explicable in terms of the lower content of oxazoline units.

The gel permeation chromatogram of an ethanol solution of copolymer fraction 2 showed that this polymer had a unimodal molecular weight distribution. The retention volume of this polymer solution is similar to that of a solution of poly (ethylene oxide), having a molecular weight of a few thousand, in the same solvent.

References

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