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Polymer chemistry. Part 4*. Partly fluorinated polyethers as additives for surface modification

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Abstract

The polymerisation of methyl methacrylate has been studied with mixtures containing variable amounts of fluorinated polyethers as additives. The resultant samples of poly(methyl methacrylate) (PMM) were studied by ESCA spectroscopy and a remarkable degree of surface segregation was observed. An enhanced concentration of the fluorinated component was observed which varied little with the composition of the polymerisation mixture. Similar effects were observed when additions were made to a commercial paint.

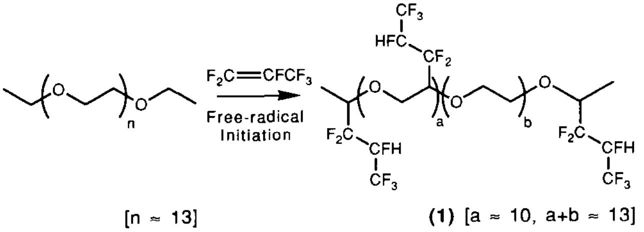
Introduction

We have developed useful methodology for the synthesis of partly fluorinated polyethers by a process which involves the free-radical grafting of fluorinated alkenes on to a variety of polyethers [2, 3] (see Scheme 1).

Fluorine-containing organic systems have highly unusual properties, including unique surface characteristics, and recent work has revealed a tendency for surface segregation of partly fluorinated systems [4, 5]. Consequently, we have investigated the effect of our novel fluorinated polyethers **1** on the surface composition of 'doped' poly(methyl methacrylate) (PMM).

Experimental

Solutions of poly(methyl methacrylate) (PMM) (5.7 g) in acetone (57.6 g) and **1** (2.5 g) in acetone (9.7 g) were prepared and combined in a number



Scheme 1.

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*For Part 3, see ref. 1.

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of samples of varying constitution as detailed in Table 1. Approximately 1.5 ml was withdrawn from each sample and deposited on a glass slide with rounded edges to give a thick film with an approximate area of 4 cm^2. Acetone was allowed to evaporate from the films, first under atmospheric conditions, then under high vacuum.

Further samples were prepared by mechanically mixing ICI Dulux 'Pure Brilliant White Gloss Finish' paint with varying amounts of **1** on a glass slide and allowing to dry.

X-Ray photoelectron spectroscopy (ESCA) measurements were taken on a Kratos ES300 surface analysis instrument (base pressure $\approx 6 \times 10^{-10}$ Torr). Mg Kα radiation was used as the excitation source with electron detection in the fixed retarding ratio (FRR) analyser mode. ESCA spectra were acquired at an electron take-off angle of 30° from the surface normal. Data accumulation and component peak analysis were performed on an IBM PC computer, using Gaussian fits with fixed FWHM and linear background subtraction.

Discussion

We have taken solutions of poly(methyl methacrylate) (PMM) with added **1** in acetone and allowed the solvent to evaporate under standard conditions on a glass slide. The poly(methyl methacrylate)–air interface of a series of samples with decreasing amounts of **1** as dopant were investigated by electron spectroscopy for chemical analysis (ESCA). One of the beneficial effects of fluorine compounds for ESCA is the separation of C_{1s} binding energies of, for example, a CF_3 group, from the normal range of hydrocarbon systems. In this case, the C_{1s} components arising from CF_2 and CF_3 were clearly discernible without curve resolution (see Fig. 1) and hence a comparison of the ratio of $C_{1s}(CF_3)/C_{1s}(\text{total})$ provides a very definitive indicator of the changes of surface composition occurring in the series.

The results of such a study are illustrated in Fig. 2 and reveal a quite dramatic extent of surface segregation. Remarkably, there was little discernible change in the surface composition until as little as 1% of **1** was contained

TABLE 1

Solutions of **1** in poly(methyl methacrylate) (PMM)

Wt. of PMM solution (g)	Wt. of PMM (g)	Wt. of solution (g)	Wt. of **1** (g)	% **1** in film
8.30	0.747	4.48	0.923	55.3
8.33	0.750	1.12	0.231	23.5
8.50	0.765	0.48	0.099	11.5
8.53	0.768	0.24	0.049	6.0
8.62	0.776	0.14	0.029	3.4
8.96	0.806	0.04	0.008	1.0

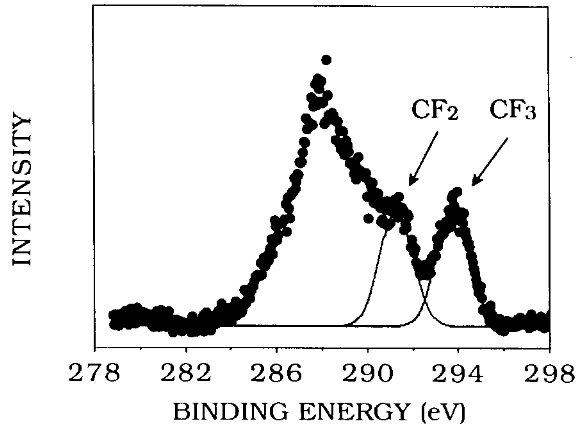

Fig. 1. ESCA plot of binding energy versus intensity for samples of 1 on poly(methyl methacrylate).

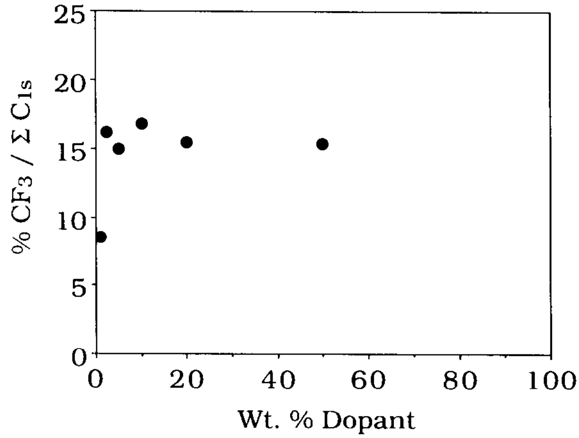

Fig. 2. Plot of $C_{1s}(CF_3)/\Sigma C_{1s}$ versus % 1 on poly(methyl methacrylate) surfaces.

in the poly(methyl methacrylate). We have also carried out a similar series of experiments using a commercial paint and comparable results were obtained from the ESCA measurements.

Thus, polyethers containing hexafluoro-n-propyl groups show a clear tendency towards migration to the air–poly(methyl methacrylate) interface, rather than towards the bulk or the interface with glass. Other workers [5] have noted a tendency for polysiloxanes containing some fluorocarbon groups to migrate in poly(methyl methacrylate) matrices. However, the direction of migration in that case depended on the size of the fluorocarbon group. Trifluoropropyl groups induced migration to the glass–poly(methyl methacrylate) interface whereas, like our observations, larger groups promoted migration to the air–poly(methyl methacrylate) interface.

This demonstrates the feasibility of adding modified polyether, or related materials, to a variety of paints or resins and obtaining some of the effects of partial fluorination at the surface, without the expense of a major concentration in the bulk. It is to be anticipated that desirable effects, such as enhanced weatherability, including resistance to biochemical degradation and UV resistance would arise from the use of such additives.

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