In reference 6, the orientation of the chemical shift tensor of the carbons of diethylether with respect to the molecular bonds is not given. In the present study, the reasonable assumption of a symmetrical distribution of the C–0 bonds about the molecular axis leads to an orientation of the shielding tensor. It is different in a CH_2–0 group and in a –CH_2– one[8]. The strongly electronegative oxygen atom plays a determinant role. This is a good illustration of how motional effects can help for assigning orientation of chemical shift tensors.

Conclusions

These preliminary results clearly demonstrate the value of proton-decoupled ^{13}C n.m.r. lineshape analysis for the description of intramolecular dynamics in polymer solids. It is particularly noticeable that the increasing rate of rotation of the phenyl rings about their C_1–C_4 axis is closely related to the apparition of the smectic phase of the polyester.

However, it also appears that ^{13}C lineshape investigation is complementary to ^{13}C $T_{1\rho}$ measurements. When the interpretation of ^{13}C $T_{1\rho}$ data in terms of molecular motions is valid[1], ^{13}C lineshape analysis gives more information about the nature of the motional processes, although less about their rates. But, in some cases, such as anisotropic reorientation and low *rf* fields, the molecular motion contribution to the ^{13}C $T_{1\rho}^{-1}$ may be hidden by spin–spin depolarization effects[1]. In such a case, a ^{13}C lineshape study becomes an attractive alternate to ^{13}C $T_{1\rho}$ measurements.

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Chemical modification of chloromethylated crosslinked polystyrene *via* phase transfer catalysed Wittig reactions

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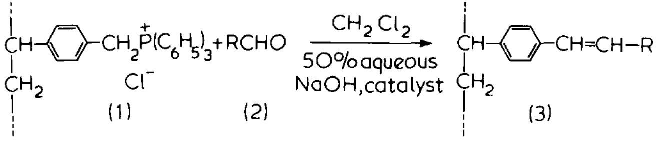
Introduction

The recent considerable interest in polymer-supported reagents, catalysts, and protecting groups[1] and in chemically active stationary phases for chromatography[2] has, in turn, led to renewed interest in the preparation of chemically modified crosslinked polystyrenes[3]. One method of obtaining a polymer with the required functional groups is to attach appropriate small molecules by covalent bonds to a preformed polystyrene[4]. We wish to report a method of this type which proceeds at ambient temperatures and which results in the small molecules being attached to the polymer by bonds which are stable to both acid and base. The key step is a phase transfer catalysed Wittig reaction between a polymer containing phosphonium salt residues (1) and an aldehyde (2) to give a polymer containing residues (3). Until recently phase transfer catalysed reactions have only occasionally been used in polymer chemistry[5,6], although they have been used extensively in organic chemistry for several years[7].



Experimental

The following procedures are typical.

Preparation of the polymer containing phosphonium salt residues (*1*). Chloromethylated 2% crosslinked polystyrene[8] (10.09 g, 3.57 mmol of Cl per g) was treated with triphenylphosphine (15.01 g) in chlorobenzene (50 ml) at reflux temperature for 60 h. After cooling the polymer was filtered off, washed successively with benzene and ether, then dried to constant weight (19.50 g). By phosphorus analysis it contained 1.81 mmol of phosphorus per g. Chloromethylated polystyrene has strong infra-red bands as 1270 and 680 cm^{-1} but the product had only very weak bands at these positions; it had new strong bands at 1440 and 1000 cm^{-1}.

Wittig reaction with ferrocene-carboxaldehyde. The above polymer (2.00 g), ferrocene-carboxaldehyde (784 mg), methylene chloride (8 ml), 50% aqueous sodium hydroxide (8 ml), and cetyltrimethylammonium bromide (150 mg) were vigorously stirred under nitrogen at 20° for 36 h. The polymer beads were filtered off and washed successively with aqueous tetrahydrofuran, tetrahydrofuran, and ether then dried. The red-brown product (1.39 g) had a strong infra-red band at 960 cm^{-1}, but no bands at 1440 and 1000 cm^{-1}. By elemental analysis it contained 9.0% iron, corresponding to 1.61 mmol per g of residues (9).

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Table 1 Phase transfer catalysed Wittig reactions[a]

Polymer[b]	Carbonyl compound (2)	Mol ratio of (2) to (1)	Reaction time (h)	Yield of Wittig reaction[c]	*D.F.* of Polystyrene[d]
1	none	–	60	0	0.44[e]
2	*p*-Nitrobenzaldehyde	1.0	23	49	0.22
2	*p*-Diphenylphosphinyl-benzaldehyde	1.0	48	80	0.36
1	Thiophen-2-aldehyde	1.0	70	83	0.37
2	Ferrocene-2-carboxaldehyde	1.0	36	62	0.28
2	Citronellal (5)	1.5	17	41	0.18
2	Formaldehyde	~17	60	13[f]	0.06
1	4-t-Butylcyclohexanone	1.2	72	0	0
1	Thiophen-2-aldehyde and *p*-Nitrobenzaldehyde	0.7 0.7	48	65 27	0.29 0.12

[a] See Experimental section for a typical reaction procedure

[b] 1 = 1% Crosslinked polystyrene containing 1.87 mmol of residues (1) per g
2 = 2% Crosslinked polystyrene containing 1.81 mmol of residues (1) per g

[c] Unless indicated otherwise the yield was determined by appropriate elemental analyses and/or weight changes. The remainder of the residues (1) were hydrolysed to residues (8)

[d] D.F. = Degree of Functionalization. Unless indicated otherwise, this is the fraction of the phenyl residues of the polystyrene converted into residues (3)

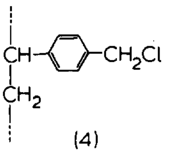
[e] Fraction of phenyl residues of polystyrene converted into residues (8)

[f] By addition of bromine and elemental analysis of the product

Results and discussion

Treatment of chloromethylated 2% crosslinked polystyrene[8] with triphenylphosphine in chlorobenzene at reflux temperature for 60 h converted essentially all the chloromethyl residues (4) into phosphonium salt residues (1). The Wittig reactions were carried out by vigorously stirring this polymer with various aldehydes (2) in methylene chloride and 50% aqueous sodium hydroxide at 20° in the presence of cetyltrimethylammonium bromide as the phase transfer catalyst. In the absence of the latter the reactions were much slower.

A selection of our results is outlined in *Table 1*. It is clear that the method allows the ready preparation of crosslinked polystyrenes with a variety of pendant groups (3). These include a polymer with phosphine groups (6) which could be useful for supporting transition metal complex catalysts[9], and a polymer with styryl residues (7) which could be used for preparing graft polymers[10]. By using an equimolar mixture of thiophen-2-aldehyde and *p*-nitrobenzaldehyde, a polymer containing both thienyl and *p*-nitrophenyl residues (mol ratio 70:30) was obtained.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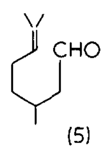
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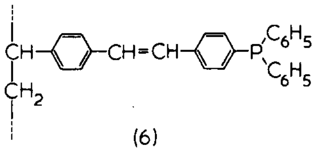
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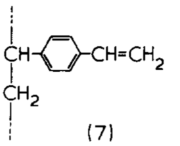
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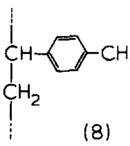
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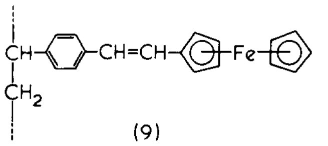
(9)

Although all the phosphonium salt residues (1) reacted, not all of them took part in the Wittig reaction. As in other phase transfer catalysed Wittig reactions[5,11], a portion of the phosphonium salt was hydrolysed to give a phosphine oxide and a hydrocarbon. In the present case this led to the formation of residues (8). Thus, treating the polymer with alkali in the absence of a carbonyl compound gave a product which was shown by ^{13}C n.m.r. spectroscopy to contain residues (8). The latter are unlikely to interfere in applications of the polymers. 4-t-Butylcyclohexanone, unlike the aldehydes, was insufficiently reactive to compete with the hydrolysis reaction and little or no olefin was formed with this substrate.

In summary, phase transfer catalysed Wittig reactions provide a versatile method for the preparation of crosslinked polystyrenes with a wide range of pendant groups. The reactions can be carried out at ambient temperatures and do not need dry solvents or dry reagents[4]. If necessary more than one pendant group can be introduced in the same reaction. We are currently extending the above method to the introduction of other pendant groups and to the modification of linear polystyrenes.

Acknowledgements

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