Synthesis of telechelic methyl methacrylate and styrene oligomers with fluorophenyl ketone end groups by the ozonolysis of copolymers containing 4-fluorophenyl butadiene units

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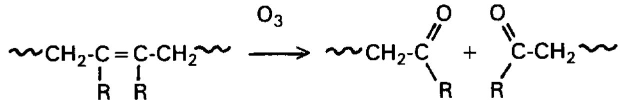
2,3-Di-(4-fluorophenyl)buta-1,3-diene has been prepared and copolymerized with methyl methacrylate and with styrene (ST) by a radical mechanism. In both cases, cleavage of the residual carbon–carbon double bonds of the diene units in the copolymer with ozone leads to telechelic oligomers with 4-fluorophenyl ketone end groups. ^{19}F n.m.r. spectra of the copolymers and oligomers show that the diene units are incorporated predominantly in 1,4-configurations with little or no 1,2-enchainment. Also, a ST–2-(4-fluorophenyl)buta-1,3-diene copolymer has been prepared and cleaved by ozonolysis to give an oligomer with both 4-fluorophenyl ketone and carboxylic acid end groups. In this system also, the ^{19}F n.m.r. spectra of the copolymer and oligomer show that the diene is incorporated almost exclusively in the 1,4-configuration.

(Keywords: copolymers; ozonolysis; telechelic oligomers; styrene; methyl methacrylate; 4-fluorophenylbuta-1,3-dienes)

INTRODUCTION

Telechelic oligomers may be prepared by the oxidative cleavage of polymers and copolymers[1–3]. For example, ozonolysis of isobutene–diene copolymers has been shown to give oligoisobutenes with terminal ketone and/or carboxyl groups depending upon the structure of the diene component. Recently we have extended the ozonolysis procedure to prepare acrylic oligomers with terminal ketone, carboxyl and hydroxyl groups from acrylic copolymers containing a variety of diene units[4,5]. The essential chemistry is shown below.



$$\sim\sim CH_2\text{-}\underset{R}{C}=\underset{R}{C}\text{-}CH_2\sim\sim \xrightarrow{O_3} \sim\sim CH_2\text{-}\underset{R}{\overset{O}{C}} + \underset{R}{\overset{O}{C}}\text{-}CH_2\sim\sim$$

Prerequisites for obtaining oligomers with high end-group functionality by the route indicated are that the parent copolymer must have a high molar mass and that the diene must be incorporated predominantly in the 1,4-configuration. The presence in a copolymer of a significant number of 1,2-diene units will result, after ozonolysis, in oligomeric fragments with additional (and generally unwanted) side-group functionality. However, although radical homopolymerizations of dienes lead to polymers containing significant amounts of 1,2-units (e.g. polybutadiene prepared by radical polymerization at 50°C contains 19% such units[6]) radical copolymers of dienes, particularly with acrylic monomers, appear to have few such units when the diene is present in only relatively small amounts. Thus, Pham *et al.* could not detect, by n.m.r. spectroscopy, 1,2-diene units in acrylonitrile–butadiene copolymers containing only low levels of diene units[7]. More recently we have shown that there are no 1,2-diene units detectable by n.m.r. in copolymers of methyl methacrylate (MMA) with butadiene and 2,3-dimethylbutadiene in which the diene contents are $\leqslant 8$ mol%[4]. Only in copolymers of MMA with 2,3-diphenylbutadiene have we been able to detect the presence of 1,2-diene units, and then at a concentration of no more than 5% diene units[4]. Thus, the diene copolymer route, on current evidence, affords telechelic oligomers in which at least 95% of the functionality occurs at the chain ends.

The aim of the work described here was to investigate the possibilty of preparing MMA and styrene (ST) telechelic oligomers with activated aryl halide end groups by the ozonolysis of copolymers of MMA and ST with 4-fluorophenyl butadienes. In particular, the fluorine atoms act as useful probes for ^{19}F n.m.r. studies of the configurations of the diene units in the copolymers and for confirmation of the presence of the desired types of end group. Also, such telechelic oligomers, if they can be made in sufficient quantity, have the potential to be chain extended via nucleophilic aromatic substitution reactions to give novel block copolymers.

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EXPERIMENTAL

Synthesis of 2,3-di-(4-fluorophenyl)buta-1,3-diene (DFB)

2,3-Di-(4-fluorophenyl)butane-2,3-diol was prepared by reaction of 4-fluoroacetophenone (120 g, 1.15 mol) with an aluminium–mercury amalgam[8] in dichloromethane with subsequent acid hydrolysis and recrystallization of the product from hexane. The pinacol so formed (67 g, 55% yield, m.p. 113°C) was heated overnight ($\sim$15 h) with $KHSO_4$ at 150°C in the presence of a small amount of 4-tert-butyl catechol as a radical inhibitor. The diene was then extracted with 40/60 petroleum ether and purified by passing the solution down an alumina column. The product was obtained as needle-shaped crystals which were further purified by recrystallization from methanol (3 g, 2.5% yield, m.p. 56–57°C). The ^1H n.m.r. spectrum of the product exhibits the expected peaks from olefinic protons at 5.31 and 5.80 ppm, relative to tetramethylsilane (TMS), and the ^{19}F n.m.r. spectrum shows a single peak at -1.6 ppm relative to fluorobenzene.

Synthesis of 2-(4-fluorophenyl)buta-1,3-diene (MFB)

4-Fluoro-α-methyl styrene was washed with aqueous NaOH and distilled under reduced pressure. This starting material (50 g, 0.38 mol) was mixed with CCl_4 (25 ml) and *N*-bromosuccinimide (40 g) and the mixture was refluxed with the aid of the heat from a 250 W lamp, the light of which initiated the bromination. When most of the *N*-bromosuccinimide had dissolved, the solution containing the 4-fluorophenyl-α-bromomethyl styrene (extremely lachrymatory!) was filtered and triphenylphosphine (100 g) and CCl_4 (225 ml) were added. The solution was stirred for 14 h. The solid phosphonium salt was filtered off, washed with CCl_4 and dissolved in CH_2Cl_2. Formalin (75 ml), with 50 ml of 80% aqueous NaOH solution, were added slowly to the solution in CH_2Cl_2 and the mixture was stirred. After 1 h, the organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. The solvent was then removed on a rotary evaporator. The residue was refluxed with 60/80 petroleum ether and filtered to remove undissolved material. The petroleum ether was removed on a rotary evaporator and the residue distilled under reduced pressure to give a colourless product (3.7 g, 4% yield). The ^1H n.m.r. spectrum of the product shows a complex pattern with peaks from olefinic protons visible at 4.8–5.4 ppm and with aromatic proton peaks at 6.2–7.4 ppm. The integrated signals show the required ratio of methyl and methylene to aromatic protons (5:4). [A similar ^1H n.m.r. spectrum is obtained from a sample of 2-phenylbuta-1,3-diene prepared by a synthetic method identical to the one described above (4 g, 8% yield); this spectrum contains peaks from olefinic methylene protons at 4.9–5.3 ppm and an olefinic methine peak at 6.3–7.8 ppm split into two doublets.]

Other materials

MMA and ST (Aldrich) were washed with aqueous NaOH (10% w/v) prior to use to remove radical inhibitors (hydroquinone and 4-tert-butyl catechol, respectively), dried over anhydrous Na_2SO_4 and then distilled under reduced pressure.

Copolymerizations

Radical copolymerizations of MMA with DFB, and of ST with DFB and with MFB, were carried out at 60°C in ampoules under vacuum using benzene as a diluent (overall monomer concentration 5 mol l^{-1}). Benzoyl peroxide (1 g l^{-1}) was used as the initiator. The copolymers were recovered by precipitation in methanol. The feed ratios used for the preparation of the copolymers are given in *Table 1*. Conversions were, in all cases, kept below 10 wt% to ensure production of relatively homogeneous copolymers.

Ozonolysis of the copolymers

Ozonolysis was performed by passing a stream of O_2/O_3 from an electric discharge-type O_3 generator

Table 1 Analytical data for the copolymers and the oligomers derived from them

	$\bar{M}_n$			Mol. fraction of MMA or ST		Elemental analysis (wt%)					
						Found			Theor.[b]		
Sample	Exp.	Theor.[a]	$\bar{M}_w/\bar{M}_n$	Feed	Copolymer	C	H	F	C	H	F
MMA–DFB											
Copolymer 1	92 860	–	1.6	0.96	0.94	–	–	–	62.6	7.6	2.1
Oligomer 1	12 300	1805	1.8	–	–	–	–	–	61.4	7.5	2.1
Copolymer 2	9140	–	4.1	0.90	0.89	63.9	7.5	3.3	64.5	7.3	3.6
Oligomer 2	2310	1047	1.4	–	–	58.7	6.7	2.5	62.5	7.1	3.5
ST–DFB											
Copolymer 3	23 450	–	1.6	0.95	0.89	90.4	7.4	2.5	89.4	7.1	3.5
Oligomer 3	2280	1152	2.0	–	–	–	–	–	86.8	6.9	3.4
Copolymer 4	11 190	–	1.5	0.90	0.79	–	–	–	87.4	6.6	6.0
Oligomer 4	860	661	3.4	–	–	–	–	–	83.1	6.3	5.7
ST–MFB											
Copolymer 5	6380	–	3.6	0.90	–	82.0	6.8	6.3	–	–	–
Oligomer 5	790	–	1.8	–	–	61.8	5.8	4.6	–	–	–

[a] Predicted from measured copolymer compositions assuming that all diene units are in a 1,4-configuration and that all are cleaved during ozonolysis

[b] For copolymers, calculated using measured compositions; for oligomers, calculated assuming that all diene units are in a 1,4-configuration and that all are cleaved during ozonolysis to give fluorophenylketone end groups (DFB) or fluorophenylketone plus carboxylic acid end groups (MFB)

through a solution of copolymer (~1 g) in $CHCl_3$ (25 ml) at an overall flow rate of 45 l h^{-1} for ~1 h at 0°C. (The rate of delivery of O_3 under these conditions was 1.74 g h^{-1} as determined by titration of iodine liberated from a standard aqueous solution of KI.) The polymeric ozonides so formed were cleaved *in situ*[9] by addition of a solution of KI in acetic acid followed by stirring for ~2 h. (However, ^{13}C n.m.r. studies subsequently showed that this second step was not always necessary as the ozonide was unstable at room temperature. Thus, the spectrum of the cleaved copolymer was invariably the same regardless of whether or not the oxidative step was used.) The organic layer was washed with water, dried over anhydrous Na_2SO_4 and the solvent removed on a rotary evaporator to leave the desired oligomer. In all cases, the yield of oligomer was 90 wt% or more of the starting copolymer.

N.m.r. and g.p.c. analysis of the copolymers

^1H n.m.r. spectra were recorded at 60 MHz on solutions in $CDCl_3$ (10% w/v) on a Jeol JNM-PMX60 spectrometer using TMS as an internal reference.

^{13}C n.m.r. spectra were recorded at 25 MHz also on 10% w/v solutions in $CDCl_3$ using a Jeol FX100 spectrometer. ^{19}F n.m.r. spectra were recorded at 94 MHz on 10% w/v solutions in $CDCl_3$ using a Jeol FX100 spectrometer with fluorobenzene as external reference. Typical conditions for recording the ^{13}C spectra were: spectral width, 5 kHz; pulse width, 12 μs; acquisition time, 0.8 s; pulse delay, 2–10 s; number of pulses, 10^3–10^4. Typical conditions for recording the 94 MHz ^{19}F spectra were: spectral width, 2 kHz; pulse width, 4.8 μs; acquisition time, 1.02 s; pulse delay, 2.0 s; number of pulses, 10–10^3.

Number-average molar masses ($\bar{M}_n$) and polydispersities ($\bar{M}_w/\bar{M}_n$) were determined by g.p.c. using a Waters 510 chromatograph equipped with a Waters refractive index detector and two 60 cm columns packed either with 10 μm PL gel beads of mixed pore size (for copolymer analysis) or with 5μm PL gel beads with pore sizes of 500 and 1000 Å, respectively (for oligomer analysis). Tetrahydrofuran was used as solvent at a flow rate of 1 ml min^{-1}. The columns were calibrated with a set of polystyrene standards of narrow molar mass distribution.

RESULTS AND DISCUSSION

MMA–DFB copolymers and the oligomers derived from them

The compositions of the MMA–DFB copolymers, copolymers 1 and 2 (see *Table 1*) were determined by ^1H n.m.r., the relative amounts of the incorporated diene being determined by integration of the phenyl proton signals and comparison with the integral of the signals from the methacrylate α-methyl protons. For copolymer 2, the composition is confirmed by the close agreement between the calculated and measured C, H, F analysis figures. G.p.c. analysis shows that on increasing the amount of diene, the M_n of the copolymer is substantially reduced (see *Table 1*). We believe this to be a consequence either of enhanced chain termination and/or, more probably, relatively slow chain propagation by DFB-ended radicals. Although there are no data on propagation (k_p) and termination (k_t) rate constants for polymerizations of DFB, k_p has been measured for butadiene itself and is about a factor of four smaller than k_p for ST which in turn is 5–10 times smaller than that of MMA at similar temperatures[10]. It seems likely to us that the reactivity of DFB will be similar to that of butadiene and thus lower than that of either MMA or ST.

The ^{13}C n.m.r. spectrum of copolymer 2 is shown in *Figure 1*. Of particular interest are the signals between 114 ppm and 166 ppm; these can be assigned to olefinic and aromatic carbons of the monomer units derived from DFB. Precise assignments are not clear except that the large signal at 114 ppm also occurs in DFB monomer and so presumably is from aromatic carbons. Also not clear from the carbon spectrum is whether or not the majority of the diene units are in *cis*- and *trans*-1,4-configurations or whether there are significant quantities of 1,2-DFB units (olefinic methylene carbon signals from 1,2-units would be expected at around 114 ppm, i.e. to overlap with the aromatic carbon signal)[11].

That 1,2-diene units are probably largely absent in the copolymers is shown by their ^{19}F n.m.r. spectra (*Figure 2*). These spectra contain only two large fluorine signals emanating from the polymer, at −2.6 and −3.2 ppm relative to fluorobenzene, which are assigned to *cis*-1,4 and *trans*-1,4-DFB units, respectively; there is no signal downfield from fluorobenzene as would be expected if any 1,2-DFB units were present. Thus it appears that these copolymers, like those of MMA with butadiene and 2,3-dimethylbutadiene made by us previously[4] and mentioned in the Introduction, contain few, if any, 1,2-diene units.

Values of $\bar{M}_n$ for the oligomers obtained by ozonolysis of the copolymers are given also in *Table 1*. As can be seen from the data, the molar masses of the oligomers are substantially lower than those of the parent copolymers, although not as low as those predicted from the compositions of the copolymers and assuming 100% scission of the diene units. There is evidence in these data, therefore, that not all the double bonds in the copolymer

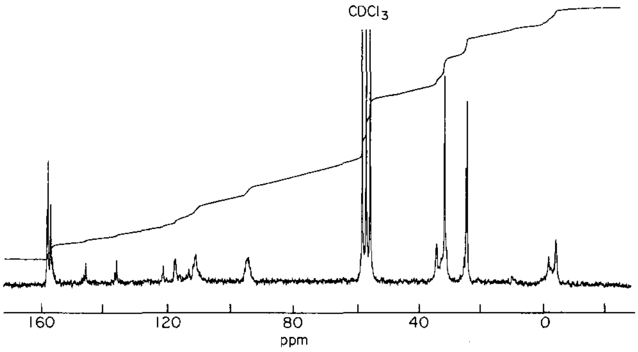


Figure 1 25 MHz ^{13}C n.m.r. spectrum of MMA/DFB copolymer 2

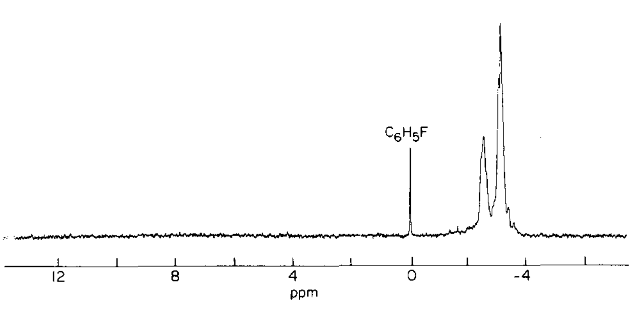


Figure 2 94 MHz ^{19}F n.m.r. spectrum of MMA/DFB copolymer 2

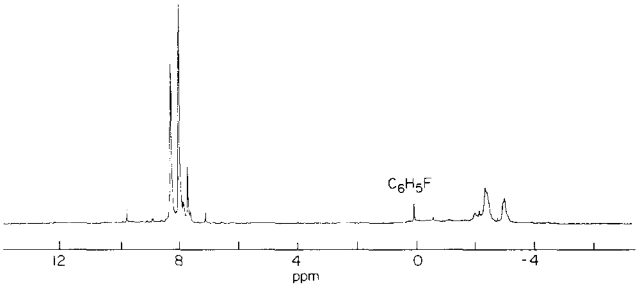
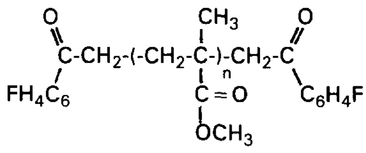


Figure 3 94 MHz ^{19}F n.m.r. spectrum of oligomer 2 (prepared from MMA/DFB copolymer 2)

backbones have been cleaved. The degrees of scission that can be calculated for copolymers 1 and 2 from the $\bar{M}_n$ values given in *Table 1* are 7.5 and 4.0, respectively. Thus, of the chains in oligomers 1 and 2, at best only 81 and 60%, respectively, will be difunctional, the remainder will be monofunctional. Similarly inefficient ozonolysis was observed earlier by us in experiments with MMA–2,3-diphenylbuta-1,3-diene copolymers[4]. Little can be deduced from the polydispersities for the copolymers or for the oligomers, except that the values for the oligomers are within the range expected (1–2) for a set of short chains made by essentially random cleavage of larger molecules[4].

That the copolymers have not been efficiently cleaved by ozonolysis is confirmed in the ^{19}F n.m.r. spectra of the oligomers which show residual signals at −2.6 and −3.2 ppm arising from residual diene units (*Figure 3*). However, the major signals in these spectra are at 7.9 and 8.2 ppm, respectively; these signals are assigned to the fluorine atoms of the fluorophenylketone groups present at the ends of the oligomer chains:



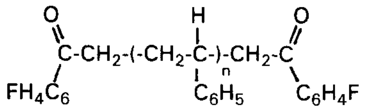
$$FH_4C_6-C(=O)-CH_2-(-CH_2-C(CH_3)(C(=O)OCH_3)-)_n-CH_2-C(=O)-C_6H_4F$$

It can be seen from the above structure that the two end groups are not equivalent and therefore that two fluorine end-group signals are to be expected. The assignment of signals at around 8 ppm to fluorophenylketone groups is confirmed by the observation that 4-fluoroacetophenone gives a ^{19}F signal at 7.75 ppm.

ST–DFB copolymers and the oligomers derived from them

The compositions of these copolymers were determined by integration of the ^{13}C n.m.r. signals at 114 ppm arising from the fluoroketone aromatic carbons and at ~40 ppm arising from aliphatic backbone carbons, and are given in *Table 1*. These compositions are not considered reliable to better than ~ ±5 mol% owing to the non-quantitative conditions under which the ^{13}C spectra were recorded and the uncertainties in determining the signal areas. However, in the case where C, H, F analysis data are available (copolymer 3), the agreement between the theoretical and the experimental values is reasonable, indicating that the copolymer composition data are not significantly in error.

The ^{19}F n.m.r. spectra of the ST–DFB copolymers are similar to those of the MMA–DFB copolymers in that they contain signals between −5 ppm and −3 ppm which are assigned to the fluorine atoms of fluorophenyl groups in *cis*- and *trans*-1,4-DFB units, although these signals are less well-resolved than the equivalent signals in the MMA–DFB copolymers (*Figure 4*). On ozonolysis of the copolymers, these ^{19}F signals are largely replaced by new signals between 7 ppm and 9 ppm (*Figure 5*) which are assigned to the fluorophenylketone end groups in:



$$FH_4C_6-C(=O)-CH_2-(-CH_2-CH(C_6H_5)-)_n-CH_2-C(=O)-C_6H_4F$$

These end-group signals, however, show rather more fine structure than the equivalent signals in the spectra of MMA oligomers 1 and 2. We believe that this fine structure arises as a consequence of the different shielding effects of *meso* and *racemic* ST–ST dyads adjacent to the end groups. That such fine structure is less evident in the end-group signals from the MMA oligomers must be an indication that the stereochemical shieldings produced by terminal *meso* and *racemic* dyads in these oligomers are roughly equivalent. A similar difference in the amount of fine structure has been seen also in the ^{13}C n.m.r. signals from 2-cyano-2-propyl end groups in poly(methyl methacrylate)s and polystyrenes initiated by azoisobutyronitrile, and has likewise been attributed to the different shielding effects of adjacent *meso* and *racemic* monomer dyads[12]. Fine structure attributable to stereochemical effects of adjacent monomer units has been seen also in ^{19}F n.m.r. signals from fluorobenzoyloxy end groups[13], ^{13}C n.m.r. signals from benzoyloxy end groups[14] and ^{1}H n.m.r. signals from t-butoxy end groups[15].

As with the MMA–DFB copolymers, increasing the amount of diene in a ST–DFB copolymer reduces its $\bar{M}_n$. Once again, we believe this to be a consequence of increased rates of termination and/or decreased rates of propagation involving DFB-ended radicals. This means

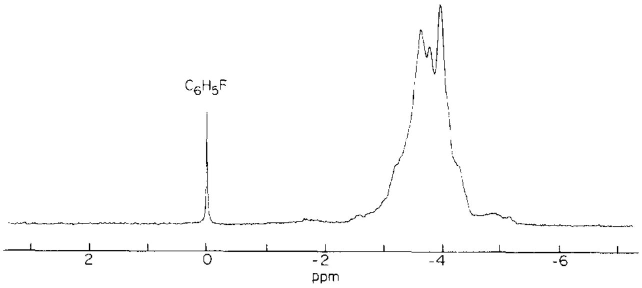


Figure 4 94 MHz ^{19}F n.m.r. spectrum of ST/DFB copolymer 4

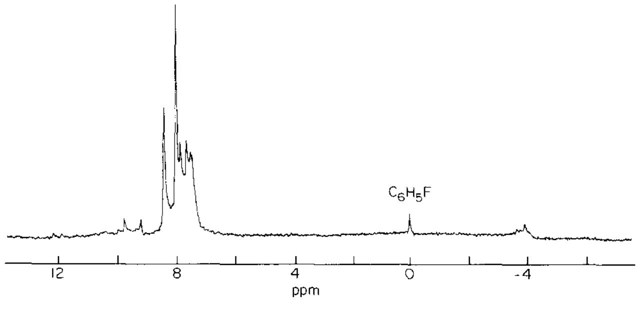


Figure 5 94 MHz ^{19}F n.m.r. spectrum of oligomer 4 (prepared from ST/DFB copolymer 4)

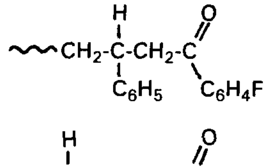
that oligomers produced from such copolymers will have rather less than the desired end-group functionality of close to 2 since each copolymer chain will contain rather few diene units. The molar mass data in *Table 1* indicate that the degrees of chain scission for copolymers 3 and 4 are 10.3 and 13.0, respectively, corresponding to 82.3 and 85.7% of the oligomers being difunctional in each case. Once again, little can be deduced from the measured polydispersities although it should be noted that the g.p.c. trace for oligomer 4 was bimodal (hence the high value of $\bar{M}_w/\bar{M}_n$), a further indication of incomplete chain scission.

ST–MFB copolymer and the oligomer derived from it

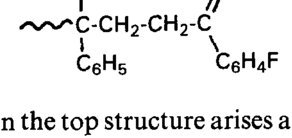
Characterization data for the one copolymer prepared from ST and MFB, copolymer 5, and for the derived oligomer are given in *Table 1*. It can be seen that ozonolysis of the copolymer produced an approximately eight-fold reduction in $\bar{M}_n$ indicating the incorporation of significant MFB in 1,4-configurations. This reduction in $\bar{M}_n$ corresponds to the production of oligomers, 77.8% of which should be difunctional. The polydispersity of the oligomer is within the range expected. Once again, a low molar mass was obtained for the copolymer indicating, we believe, high rates of chain termination and/or restricted, or retarded, chain propagation for the diene-ended radicals.

Unfortunately, the ^{13}C and ^{1}H n.m.r. spectra recorded on the copolymer were insufficiently well-resolved to allow a reliable estimate of the composition of the copolymer but it was expected that the composition would not differ much from that of the feed from which the copolymer was prepared, i.e. 0.9 mol fraction of ST. However, the C, H, F analysis data for this copolymer (see *Table 1*) indicate a rather lower ST content of around 0.6 mol fraction [for such a copolymer, the expected analysis figures (wt%) are: C, 82; H, 6.8; F, 6.3].

Ozonolysis of ST–MFB copolymers should give rise to ST oligomers with 4-fluorophenylketone functionality at one chain end and carboxyl functionality at the other. The ^{19}F n.m.r. spectrum of the copolymer gives a broad unresolved fluorine signal centred at −3.6 ppm, i.e. in a similar position to the fluorine resonances in the MMA–DFB and ST–DFB copolymers. We take this to indicate that the ST–MFB copolymer does indeed contain diene units predominantly in 1,4-configurations. In the ozonolysed (oligomeric) material, the ^{19}F n.m.r. resonances are better resolved and give rise mainly to two large signals between 7 ppm and 9 ppm, i.e. are consistent with the presence, once again, of 4-fluorophenyl end groups. The fact that, in this oligomer also, the fluorine end-group signals contain two major components is probably an indication that two different 4-fluorophenylketone end groups are present:



$$\sim\!\sim CH_2-\underset{C_6H_5}{\overset{H}{C}}-CH_2-C(=O)-C_6H_4F$$



$$\sim\!\sim \underset{C_6H_5}{\overset{H}{C}}-CH_2-CH_2-C(=O)-C_6H_4F$$

The end group in the top structure arises as a consequence of addition of a propagating styryl radical to C4 of MFB (i.e. tail addition), whilst that in the bottom structure arises from addition to C1 of MFB (i.e. head addition).

In addition to 4-fluorophenyl ketone end groups, the oligomer made from the ST–MFB copolymer would be expected to contain carboxyl end groups. That this is indeed so is confirmed by the presence of a carboxyl carbon signal at 178.3 ppm in the ^{13}C n.m.r. spectrum of the oligomer.

If, as the C, H, F analysis data suggest, copolymer 5 contains about 0.6 mol fraction of ST, then the oligomer produced from it, assuming that all diene units are in a 1,4-configuration and that all are cleaved during ozonolysis, should give the following analysis data (wt%): C, 75.0; H, 6.0; F, 5.4. It can be seen from *Table 1* that the H and F values above are close to those found experimentally but that there is some discrepancy in the C values. Also, a ST content of 0.6 mol fraction in copolymer 5 would lead to an oligomer containing, on average, 1.5 ST units per chain; such an oligomer would have an $\bar{M}_n$ of 296. This calculated molar mass is of the same order as that determined by g.p.c. although somewhat lower. However, it must be remembered that the g.p.c. molar masses are only approximate since calibration was carried out with low molar mass polystyrene standards and not with substances with similar structures to the oligomers, and also that in the isolation of the oligomers the lowest molar mass fraction may be removed with the solvent during work-up.

CONCLUSIONS

It has been shown that the method described previously, whereby telechelic acrylic oligomers are produced by the ozonolysis of copolymers of an acrylic or vinyl monomer with a simple diene such as butadiene, isoprene or 2,3-dimethylbutadiene[4,5], can be extended to produce oligomers from copolymers of MMA and ST with novel 4-fluorophenyl substituted butadienes. However, the molar masses of the starting copolymers are relatively low and the ozonolyses do not go to completion. These two factors together lead to the conclusion that the oligomers have rather less than the desired degree of end functionality; in fact, end functionalities calculated from the molar mass data range from 1.6 to just below 1.9. These levels of functionality are clearly not ideal but might suffice for the production of various multiblock copolymers.

The fluorine atoms in the dienes have proved to be useful labels for ^{19}F n.m.r. studies of copolymer structure and of the structures of the end groups in the oligomers derived from them. We have shown that both DFB and MFB are incorporated predominantly in 1,4-configurations (as opposed to 1,2-configurations) and that the oligomers contain the expected 4-fluorophenyl ketone end groups.

Unfortunately, the low yields obtained in the preparations of the dienes, DFB and MFB (2.5 and 4%, respectively), have so far precluded the preparation of oligomers based upon them in sufficient quantities to allow any chain extension reactions to be explored. However, the other stages in the syntheses of the oligomers are reasonably efficient. Although we chose to prepare copolymers in low conversion experiments, there is no reason why such copolymerizations should not be carried out to high conversion using starve-fed emulsion polymerization techniques. Recently we have used such a technique to prepare MMA–2,3-dimethylbutadiene copolymers in 10–100 g quantities[16]. The recovery of the oligomers from the ozonolysed copolymer solutions also presents no problems, being virtually quantitative.

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