Preparation and reactions of vinyl sulphonate–vinyl acetate copolymers

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The radical copolymerization of two vinyl sulphonates, vinyl methanesulphonate (MVS) and vinyl benzenesulphonate (BVS), with vinyl acetate (VAc) was carried out to prepare vinyl sulphonate–vinyl acetate copolymers. The monomer reactivity ratios of these copolymerization systems were estimated to be r_1(VAc) = 0.66, r_2(MVS) = 0.26 and r_1(VAc) = 0.71, r_2(BVS) = 0, respectively. The MVS/VAc copolymer thus obtained was found to initiate the polymerization of 2-methyl-2-oxazoline (OXZ) to produce poly(VAc)–poly(OXZ) graft copolymer, which was subsequently converted to poly(vinyl alcohol)–poly(OXZ) graft copolymer through the saponification of the poly(VAc) segment of the parent poly(VAc)–poly(OXZ) graft copolymer.

(Keywords: vinyl sulphonate; vinyl acetate; vinyl alcohol; copolymerization; oxazoline; graft copolymer)

INTRODUCTION

Although the copolymerization technique is a common method in the synthesis of a wide variety of functional polymers, the application of the copolymerization technique has been rather limited in the production of functional poly(vinyl acetate), poly(VAc), and its saponified derivative, poly(vinyl alcohol), poly(VA). This is apparently due to the poor copolymerizability of vinyl acetate, a typical non-conjugated monomer, with the usual functional monomers like styrene or methacrylate type derivatives. Also the undesired hydrolysis of the ester functional of acrylate or methacrylate derivatives may accompany the saponification of poly(VAc) to poly(VA).

In the present study, we have attempted to develop a novel reaction system to provide functional poly(VAc) and poly(VA) derivatives by means of the copolymerization technique using new functional monomers, i.e. vinyl sulphonates. Vinyl sulphonate monomers are of interest with respect to the copolymerizability with vinyl acetate since both are similar vinyl ester type monomers. Besides, vinyl polymerization or copolymerization of these compounds can provide a polymer or copolymer with sulphonate ester groups along the polymer chain. The incorporated sulphonate ester functional is expected to undergo substitution with various nucleophilic reagents. Consequently, these polymers will be utilized as versatile reactive prepolymers in order to introduce an appropriate functional group in the polymer chain by further modification.

The polymerization behaviour of vinyl sulphonates, however, has not been studied extensively since the preliminary study on the synthesis and polymerization of these compounds by Sauer and Wilson[1]. In the present study, we will describe the results on the synthesis and copolymerization of vinyl sulphonate monomers with vinyl acetate, and the subsequent modification reactions of vinyl sulphonate–vinyl acetate copolymers to produce poly(VAc) as well as poly(VA) based graft copolymers.

EXPERIMENTAL

Reagents

Vinyl methanesulphonate (MVS) and vinyl benzenesulphonate (BVS) were synthesized by the reaction of mercuribisacetaldehyde[2] with the corresponding sulphonyl chloride as reported by Nesmeyanov *et al.*[3]: vinyl methanesulphonate, yield 26%, b.p. 72°C at 4 mmHg (lit.[3] 78°C at 6 mmHg); vinyl benzene sulphonate, yield 27%, b.p. 103°C at 1 mmHg (lit.[3] 102°C at 2 mmHg). Vinyl acetate (VAc) was supplied from Kuraray Co. and purified by the method reported earlier[4]. 2-Methyl-2-oxazoline (OXZ) was distilled over CaH_2. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Other reagents were purified by the conventional procedures.

Procedures

Copolymerization of vinyl sulphonate and vinyl acetate. A weighed amount of vinyl sulphonate, vinyl acetate and AIBN were placed in an ampoule and sealed under vacuum after being degassed. The ampoule was then placed in a thermostatted bath at 60°C for the prescribed period. The copolymer obtained was isolated and purified by reprecipitation from benzene/n-hexane.

Reaction of MVS–VAc copolymer with 2-methyl-2-oxazoline (OXZ). A typical example of the reaction of MVS–VAc copolymer with OXZ was as follows. In a 30 ml flask, 0.131 g of MVS–VAc copolymer (MVS content, 15.8 mol%) was dissolved in 3.0 ml of nitrobenzene under a nitrogen atmosphere. Then 0.13 ml of OXZ was added to the above solution and stirred for 48 h at 60°C. The reaction product was then isolated by pouring the reaction mixture into petroleum ether and purified by reprecipitation from chloroform/petroleum ether. Yield, 0.158 g.

Saponification of poly(VAc)–poly(OXZ) graft copolymer. First 0.348 g of poly(VAc)–poly(OXZ) graft copolymer (VAc:OXZ = 1.0:2.0 in monomer unit ratio)

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was dissolved in 5 ml methanol and 3.5 ml of 1.0 N NaOH/methanol was added. The reaction solution was stirred for 12 h at ambient temperature, while the reaction mixture became slightly turbid. The reaction mixture was then subjected to dialysis for 9 days through a cellulose tube (VT803, Visking Co.). The evacuation of the dialysate resulted in poly(vinyl alcohol)–poly(OXZ) graft copolymer (VA:OXZ = 1.0:0.75 in monomer unit ratio). Yield, 0.075 g.

Measurements

^1H and ^{13}C n.m.r. analyses were carried out by using either Jeol GX270 or Jeol PMX60 apparatus. The proton of $CHCl_3$ (7.30 ppm) or H_2O (4.70 ppm) was used as internal standard for the chemical shift values. I.r. spectra were taken on a Hitachi 260-10 spectrophotometer. T.l.c. measurements were carried out with either 10 cm long silica gel (Merck silica gel 60, F_{254}) or aluminium oxide (Merck aluminium oxide 60, F_{254}) plates by spotting the sample in 1.0% w/v chloroform solution. The developing solvent was either methanol/acetone (5/1 by volume) for the silica gel or water/methanol (9/1 by volume) for the aluminium oxide and iodine was the staining reagent.

RESULTS AND DISCUSSION

Copolymerization of vinyl sulphonates with vinyl acetate

Vinyl sulphonates have been reportedly synthesized by two methods, namely the addition reaction of sulphonic acid with acetylene[1] and the reaction of sulphonyl chloride with mercuribisacetaldehyde[3], respectively. In the present study, we have employed the latter method because of the easy reaction procedure as well as the alleged high yield of the product. Thus, two types of vinyl sulphonates, namely vinyl methanesulphonate (MVS) and vinyl benzenesulphonate (BVS), were synthesized with a fairly good yield and used for the following copolymerization studies.

The copolymerization of these vinyl sulphonates with vinyl acetate was carried out in bulk at 60°C with AIBN as initiator. Since vinyl acetate is regarded as a similar non-conjugated vinyl ester type monomer as the vinyl sulphonates, the good copolymerizability between these two monomers was anticipated in comparison with such conjugated type monomers like styrene or methyl methacrylate.

Table 1 Copolymerization of vinyl sulphonates with vinyl acetate[a]

Exp. no.	Sulphonate	Sulphonate feed (mol%)	Time (h)	Yield (wt%)	Sulphonate content[b] in copolymer (mol%)
1[c]	MVS	2.4	1.0	10.0	3.5
2	MVS	4.8	1.5	11.7	6.7
3	MVS	7.3	2.0	9.7	10.1
4	MVS	11.1	1.5	10.3	13.7
5	MVS	15.0	3.0	14.0	18.6
6	MVS	19.0	1.6	8.7	20.1
7	MVS	26.1	1.6	5.0	29.8
8[c]	BVS	2.2	1.5	7.0	3.5
9	BVS	3.0	1.5	8.3	4.3
10	BVS	4.9	1.6	11.1	5.7
11	BVS	6.5	2.0	10.7	7.3
12	BVS	7.6	2.0	9.3	8.7
13	BVS	10.5	3.0	10.0	13.0
14	BVS	18.9	2.0	6.7	19.4

[a] Bulk, at 60°C, AIBN 0.3 wt%
[b] Determined by ^1H n.m.r. analyses
[c] AIBN 0.2 wt%

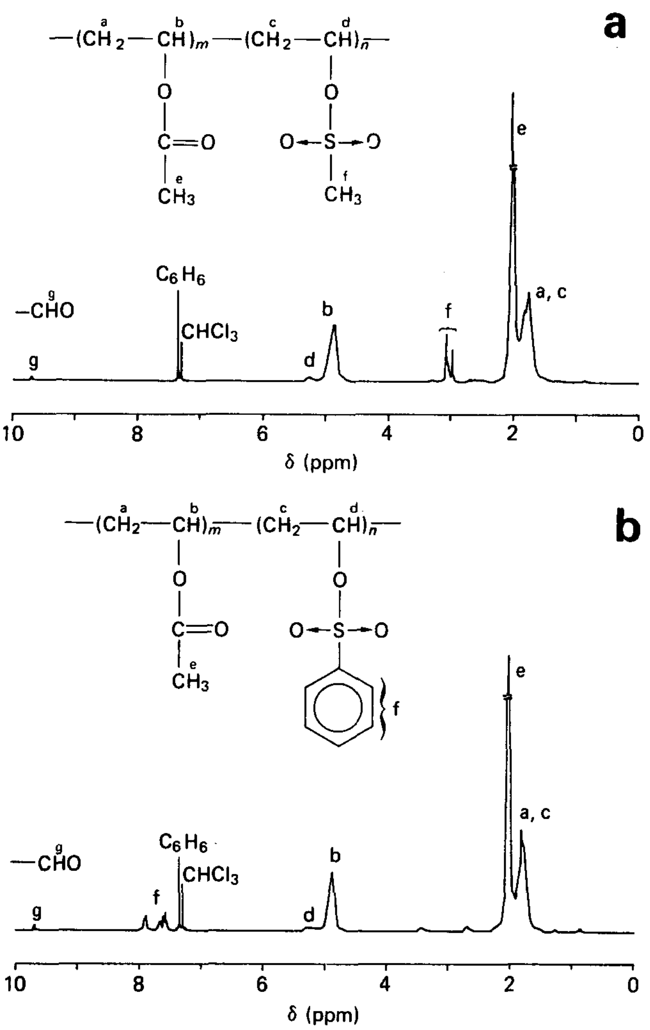

Figure 1 270 MHz ^1H n.m.r. spectra of (a) MVS–VAc copolymer (sample, exp. no. 3 in *Table 1*) and (b) BVS–VAc copolymer (sample, exp. no. 10 in *Table 1*) in $CDCl_3$

The copolymerization of each vinyl sulphonate with vinyl acetate was found to proceed as expected and the results are summarized in *Table 1*. 270 MHz ^1H n.m.r. spectra of the MVS–VAc and BVS–VAc copolymers obtained are shown in *Figures 1a* and *1b*, respectively. The signals for the vinyl sulphonate unit are visible besides those of the VAc unit in each spectrum. The methyl proton signal for the MVS unit (~3.0 ppm in *Figure 1a*) was observed to be split into a doublet, presumably reflecting the comonomer unit distribution and/or the stereoregularity. A small signal was detected at 9.7 ppm in both spectra and was assigned to the aldehyde proton, which was confirmed neither from the impurities nor from the decomposition products during the isolation procedures. Nevertheless, the mechanism of aldehyde formation during the copolymerization between vinyl sulphonates and vinyl acetate is not understood at present.

The MVS/VAc copolymer with MVS content up to 18.6 mol% and BVS–VAc copolymer with BVS content up to 13.0 mol% were white powdery solids, while MVS–VAc copolymer with MVS content more than 20.1 mol% and BVS–VAc copolymer with BVS content more than

19.4mol% were pale yellow wax-like products, suggesting a decrease of the molecular weight of the copolymer with increase of the vinyl sulphonate content.

The monomer reactivity ratios of MVS–VAc and BVS–VAc copolymerization systems were estimated through the Kelen–Tüdös plot[5] as shown in *Figures 2a* and *2b*, respectively. The monomer reactivity ratios thus obtained were $r_1(\text{VAc}) = 0.66$, $r_2(\text{MVS}) = 0.26$ and $r_1(\text{VAc}) = 0.71$, $r_2(\text{BVS}) = 0$, respectively. The resonance factor Q and electronic factor e of MVS and BVS were then estimated to be $Q(\text{MVS}) = 0.05$, $e(\text{MVS}) = -1.6$ and $Q(\text{BVS}) = 0.06$, $e(\text{BVS}) = -2.4$, using the corresponding Q and e values for VAc of 0.026 and -0.22[6], respectively. Also the $r_2(\text{BVS})$ value was presumed to be 0.01 for the approximate calculation. Both vinyl sulphonates were considered to be non-conjugated and highly electron-rich monomers.

Reaction of vinyl sulphonate–vinyl acetate copolymers

The reaction of vinyl sulphonate–vinyl acetate copolymer (vinyl sulphonate content, 5–10 mol%) with a series of amines, namely n-butylamine, diethylamine and triethylamine, was attempted under reaction conditions in which the reaction between these amines and ethyl tosylate proceeded with more than 90% conversion (in dimethylsulphoxide or acetonitrile at 40–60°C). The isolated product, however, showed no sign of nucleophilic substitution of the amine at the sulphonate ester functional of the copolymer. On the contrary, the formation of olefinic double bonds was noticed in the reaction product, presumably due to the predominant occurrence of proton abstraction from the copolymer by the amine. The present result was unexpected since it has previously been reported that the tosylation reaction of poly(vinyl alcohol) and the subsequent reactions with a series of amines did take place, even with some side reactions[7].

Then, the reaction of vinyl sulphonate–vinyl acetate copolymer with an oxazoline was examined, since the sulphonate esters reportedly react with oxazolines to produce poly(oxazoline)s[8]. In the present study, 2-methyl-2-oxazoline (OXZ) was found to undergo nucleophilic attack on the sulphonate functional in the copolymer to form the oxazolinium salt, which was subsequently reacted with excess OXZ successively to produce poly(OXZ) as the graft chain on the backbone poly(VAc) segment.

Figure 3 shows 270 MHz ^{1}H n.m.r. spectrum of the resulting poly(VAc)–poly(OXZ) graft copolymer. Besides the signals for the poly(VAc) segment, those for the poly(OXZ) segment were separately present at 3.47 ppm. The unreacted sulphonate functional was also visible at 3.09 ppm. The end group of poly(OXZ) segment was also observed at 3.00 and 4.21 ppm for the methyl sulphonate counter-anion and oxazolinium ring protons, respectively.

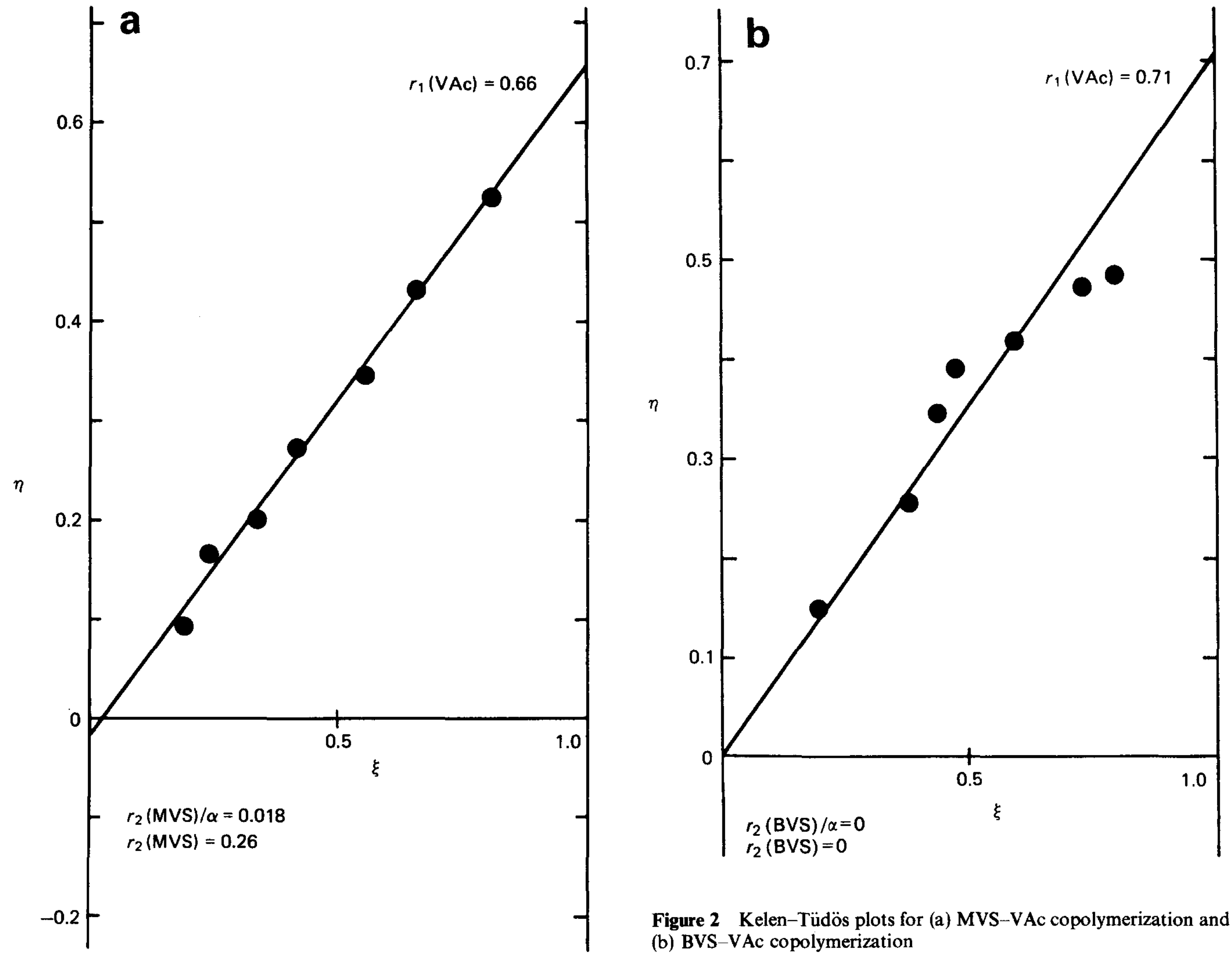

Figure 2 Kelen–Tüdös plots for (a) MVS–VAc copolymerization and (b) BVS–VAc copolymerization

The poly(VAc)–poly(OXZ) graft copolymer obtained was subjected to t.l.c. analysis, which is known to be useful to detect impurities in the graft copolymer[9]. The results are shown in *Table 2*. On the aluminium oxide plate, the water/methanol mixture, which is a good solvent for poly(OXZ) and a poor solvent for MVS–VAc copolymer, developed poly(OXZ) homopolymer but did not develop either MVS–VAc copolymer or the graft copolymer, indicating that the obtained graft copolymer was free from contamination with poly(OXZ) homopolymer. On the other hand, the methanol/acetone mixture, which is a good solvent for MVS–VAc copolymer and a poor solvent for poly(OXZ), gave two spots on the silica gel plate for the isolated poly(VAc)–poly(OXZ) graft copolymer, indicating that a portion of the parent MVS–VAc copolymer still remained in the isolated graft copolymer.

The graft reaction of OXZ on MVS–VAc and on BVS–VAc copolymer was studied at various reaction temperatures and the results are summarized in *Table 3*. For MVS–VAc copolymer, the graft reaction was found to occur at 60°C and higher but did not occur at 40°C, while the graft reaction on BVS–VAc copolymer was very sluggish even at 80°C.

The saponification of the poly(VAc) segment of the poly(VAc)–poly(OXZ) graft copolymer obtained was carried out with alkaline methanol solution, which is the usual saponification treatment for poly(VAc) homopolymer. The reaction product was then purified by dialysis

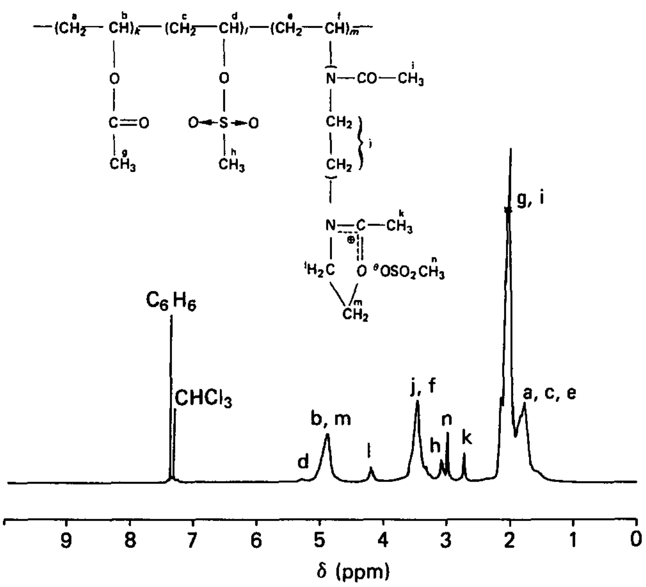

Figure 3 270 MHz ^{1}H n.m.r. spectrum of poly(VAc)–poly(OXZ) graft copolymer in $CDCl_3$ (MVS–VAc copolymer of 10.1 mol% MVS content; MVS–VAc copolymer:OXZ = 1:1 by weight, 80°C, 48 h in nitrobenzene)

Table 2 T.l.c. analysis of poly(VAc)–poly(OXZ) graft copolymer[a]

Polymer sample	R_f	
	Methanol/acetone[b]	Water/methanol[c]
MVS–VAc copolymer	1.0	0
Poly(OXZ)	0.08	1.0
Poly(VAc)–poly(OXZ) Graft copolymer	0.09, 1.0[d]	0

[a] Sample: *Table 3*, exp. no. 5
[b] 5/1 by weight on silica gel
[c] 9/1 by weight on aluminium oxide
[d] Two spots

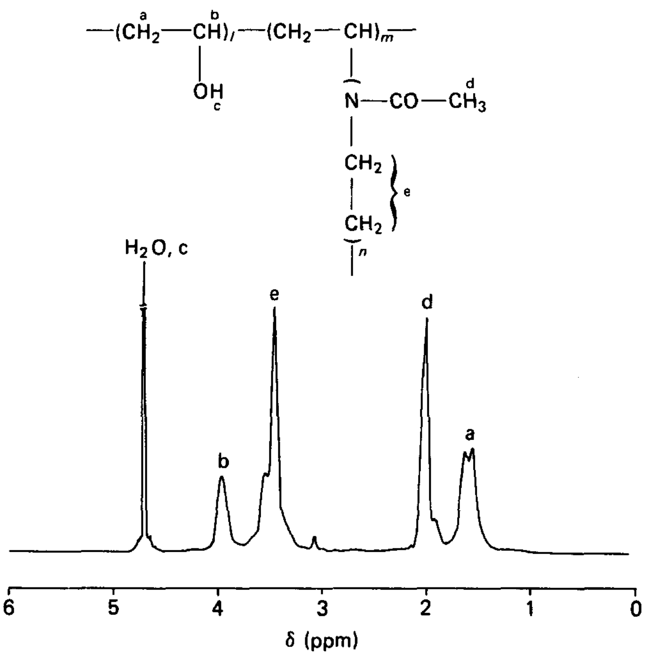

Figure 4 270 MHz ^{1}H n.m.r. spectrum of poly(VA)–poly(OXZ) graft copolymer in D_2O (see also 'Experimental')

Table 3 Reaction of vinyl sulphonate–vinyl acetate copolymer with oxazoline

Exp. no.	Copolymer sample[a]	Feed (g)			Temp. (°C)	Time (h)	Yield (g)	OXZ unit content[b] (mol%)
		Copolymer	OXZ	Nitrobenzene				
1	MVS–VAc	0.114	0.11	2.0	40	48	0.110	n.d.[c]
2	MVS–VAc	0.130	0.13	2.4	60	24	0.121	n.d.
3	MVS–VAc	0.129	0.13	2.4	60	36	0.139	9.9
4	MVS–VAc	0.131	0.13	2.4	60	48	0.158	23.1
5	MVS–VAc	0.162	3.20	3.6	80	5	0.186	18.7
6	MVS–VAc	0.143	1.00	12.0	80	6	0.112	35.9
7	MVS–VAc	0.165	3.30	3.6	80	10	0.390	63.0
8	MVS–VAc	0.162	3.20	3.6	80	15	1.320	87.1
9	BVS–VAc	0.093	0.025	0.85	60	48	–	n.d.
10	BVS–VAc	0.077	0.760	2.4	80	4	0.076	3.7
11	BVS–VAc	0.042	0.420	2.4	80	9	0 042	4.6
12	BVS–VAc	0.041	0.410	2.4	80	12	0.041	4.9

[a] MVS–VAc copolymer, MVS content 15.8 mol%; BVS–VAc copolymer, BVS content 3.2 mol%
[b] Determined by ^{1}H n.m.r. analysis
[c] Not detected

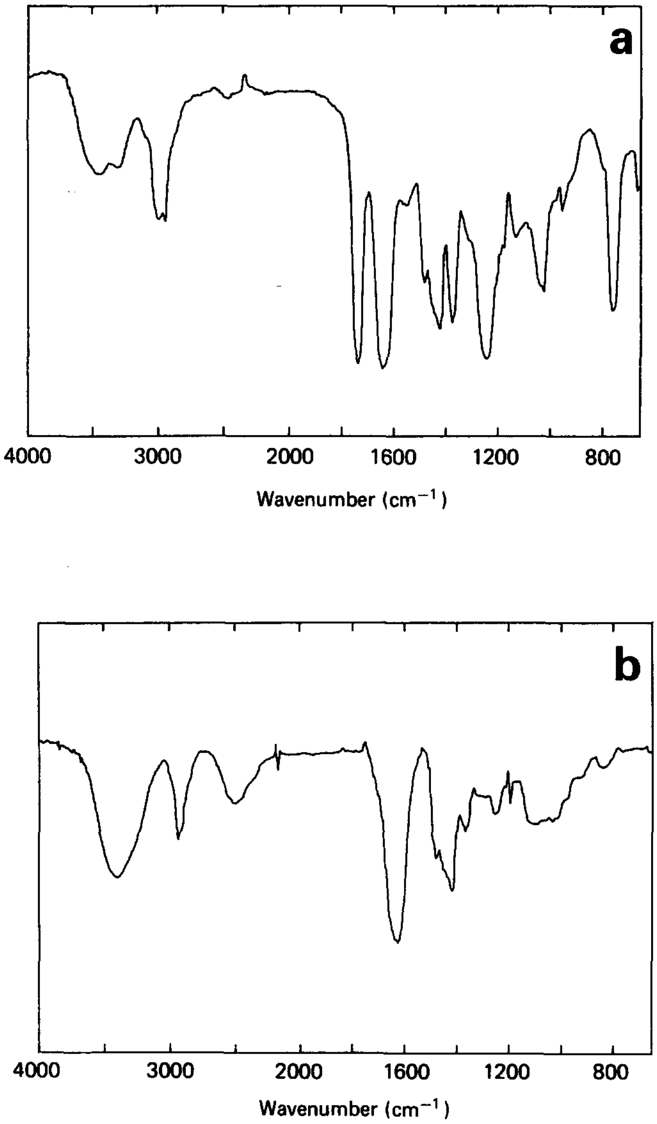

Figure 5 I.r. spectra of (a) poly(VAc)–poly(OXZ) graft copolymer and (b) poly(VA)–poly(OXZ) graft copolymer (see also 'Experimental')

through a cellophane membrane, because most of the reaction product remained soluble in methanol solution.

The 270 MHz ^{1}H n.m.r. spectrum of the purified product is shown in *Figure 4*, where the overlapping signals of poly(VA) and poly(OXZ) are visible, demonstrating the formation of poly(VA)–poly(OXZ) graft copolymer. The quantitative saponification of the poly(VAc) segment was also confirmed by i.r. spectroscopic analysis of the saponification product, namely poly(VA)–poly(OXZ) graft copolymer together with the parent poly(VAc)–poly(OXZ) graft copolymer, as shown in *Figure 5*, where the complete disappearance of the ester absorption at 1735 cm^{-1} was noticed after the saponification treatment.

Part of the poly(VA)–poly(OXZ) graft copolymer was found to be lost during dialysis, which is noticed by the decrease of the isolated yield of the saponification product. The poly(OXZ) content of the saponification product was also found to decrease, presumably because the lower-molecular-weight portion of poly(VA)–poly(OXZ) graft copolymer, which is lost during dialysis, contains the higher poly(OXZ) content.

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REFERENCES

1 Sauer, J. C. and Wilson, J. D. C. *J. Am. Chem. Soc.* 1955, **77**, 3793
2 Lutsenko, I. F. and Khomutov, R. M. *Dokl. Akad. Nauk SSSR* 1955, **102**, 97; *Chem. Abstr.* 1956, **50**, 4773b
3 Nesmeyanov, A. N., Lutsenko, I. F., Khomutov, R. O. and Duboviskii, V. A. *J. Gen. Chem. USSR* 1959, **29**, 2776 (*Zh. Obschchei. Khim.* 1959. **29**, 2817); *Chem. Abstr.* 1960, **54**, 12048b
4 Tezuka, Y., Tanaka, S. and Imai, K. *Polymer* 1986, **27**, 123
5 Kelen, T. and Tüdös, F. *J. Macromol. Sci.–Chem.* 1975, **A9**, 1
6 Young, L. J. *J. Polym. Sci.* 1961, **54**, 411
7 Reynolds, D. D. and Kenyor, W. O. *J. Am. Chem. Soc.* 1950, **72**, 1584, 1587, 1591, 1593, 1597
8 Saegusa, T. and Ikeda, H. *Macromolecules* 1973, **6**, 805
9 Inagaki, H. *Adv. Polym. Sci.* 1977, **24**, 189