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Photolysis of vinyl ketone copolymers. 4: Macromonomeric products from photolyses of copolymers of styrene and methyl acrylate with methyl vinyl ketone

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Some statistical copolymers of styrene and methyl vinyl ketone, prepared by free radical copolymerization, have been photolyzed in benzene solution using u.v. light of wavelength 300 or 350 nm. It is confirmed by n.m.r. spectroscopy that the oligomeric products so obtained have unsaturated end-groups with structures resembling that of α-methyl styrene, as would be expected on the basis of a predominantly Norrish type II photolysis mechanism. The molecular weights of the oligomers slightly exceed those expected from the copolymerization statistics, indicating probably that some slight cross-linking or repolymerization of end-groups accompanies the chain scission. Although not homopolymerizable, the unsaturated styrene oligomers produced by photolysis can be free-radically copolymerized with methyl acrylate, demonstrating that they behave as macromonomers. A copolymer of methyl acrylate with methyl vinyl ketone also gives fragments with unsaturated end-groups on photolysis, but here the accompanying cross-linking or end-group repolymerization is more dominant, leading to oligomeric products with extremely broad molecular weight distributions. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: styrene; methyl vinyl ketone; methyl acrylate)

INTRODUCTION

Previous papers in this series have described the photolysis of some methyl methacrylate (MMA)–alkyl vinyl ketone copolymers, carried out in the hope of producing, amongst the products, polymerizable oligomers (macromonomers)[1–3]. It was found, however, that photolyses of such copolymers do not proceed by a non-classical Norrish type II mechanism (δ-hydrogen atom transfer to a carbonyl group followed by β-scission and rearrangement) as had previously been proposed[4], but instead by an intuitively more reasonable Norrish type I mechanism. The type II mechanism, had it occurred, would have given acrylic-ended, and hence polymerizable, oligomeric fragments, rather than the non-polymerizable, allylic-ended fragments found in practice, which are indicative of the type I mechanism. Nevertheless, there are a number of alkyl vinyl ketone copolymers for which Norrish type II photolysis is more probable, *i.e.* copolymers of alkyl vinyl ketones with comonomers such as styrene (ST), methyl acrylate (MA), and other monomers possessing a hydrogen atom in the α-position. In copolymers with vinyl ketones, this hydrogen atom, when in a repeat unit adjacent to a vinyl ketone unit, is ideally placed (*i.e.* is γ to the ketone carbonyl group) to take part in a Norrish type II process as shown in *Scheme 1*.

Norrish type II chain scission is well documented for poly(methyl vinyl ketone)[5–7] and for analogous homopoly(vinyl ketone)s such as poly(phenyl vinyl ketone)[8–11], and has been identified as an important contributor to the photodegradation of ST–methyl vinyl ketone (MVK) copolymers[12,13] and also of copolymers of ST with phenyl vinyl ketone[10,12,14]. Although vinyl ketone copolymers, including those with ST, have been exploited commercially as photodegradable thermoplastics[15], there have been no reports, as far as we are aware, of attempts to utilize photolysis of the copolymers deliberately to produce ST oligomers with polymerizable, unsaturated end-groups, although the possibility of unsaturated oligomers produced by photolysis undergoing polymerization during the course of their production has been commented upon[6]. With all this in mind, we have characterized the oligomeric products of photolysis of some ST–MVK copolymers (and also of a copolymer of MA and MVK) particularly with regard to the nature of the end-groups and their polymerizability, and we report the results in this paper.

EXPERIMENTAL

Monomers

ST (Aldrich, 99%), MA (Aldrich, 99%) and MVK (Aldrich, 99%) were freed from inhibitors (*p-tert*-butyl catechol, hydroquinone monomethyl ether, and acetic acid plus hydroquinone, respectively) by fractional distillation under reduced pressure. All monomers were stored in a freezer at −30°C over freshly activated Linde molecular sieve type 4A until required.

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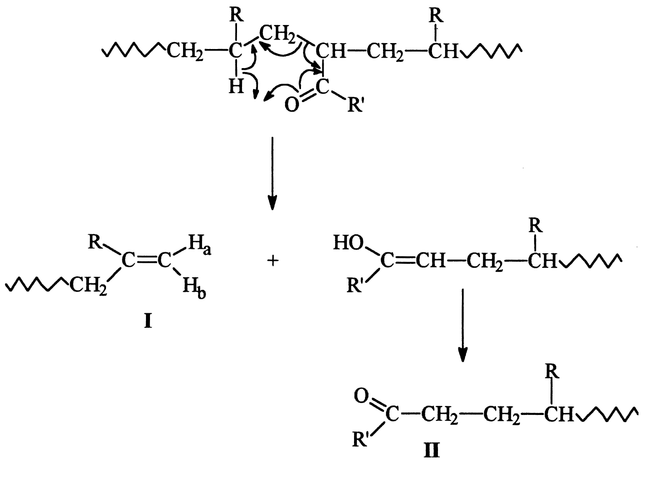


Scheme 1

Copolymer preparations

Copolymers of ST with MVK and of MA with MVK were prepared by the free radical polymerization of mixtures of the monomers under vacuum at 60°C, in benzene, using azoisobutyronitrile (AIBN) as initiator. The polymerizations were carried out in ampoules, degassed by the usual freeze–pump–thaw cycles on a vacuum line and sealed with a glass torch.

Photolyses

Photolyses of solutions of copolymers in benzene contained in degassed and sealed quartz ampoules were carried out in a Rayonet photochemical reactor using light of wavelengths 300 or 350 nm. The oligomeric products of the photolyses were recovered by removal of the solvent on a rotary evaporator, and were purified by redissolution in chloroform and precipitation in methanol. Yields of reprecipitated oligomer were all around 80% (w/w) based on the original copolymer. Similar procedures have been given in detail elsewhere[2].

Characterization of polymers and oligomers

The polymers, and oligomers derived from them, were characterized principally by ^{1}H and ^{13}C n.m.r. spectroscopy (for composition and microstructure) using Jeol FX-100, Jeol GX-400 and Bruker WH-400 n.m.r. spectrometers, and by g.p.c. in tetrahydrofuran (for the molecular weight and molecular weight distribution) using a Waters gel permeation chromatograph equipped with Polymer Laboratories PLgel™-filled columns. These procedures, too, have been given in detail elsewhere[2].

RESULTS AND DISCUSSION

ST–MVK copolymers

Reactivity ratios for the radical copolymerization of ST (M_1) and MVK (M_2) in benzene at 60°C, initiated with AIBN, were determined using the method recommended by McFarlane *et al.*[16], *i.e.* by carrying out five copolymerizations to low conversions at each of two optimized monomer feed fractions, f_1' and f_1'', and determining the fractions of ST units, F_1' and F_1'', in the resulting copolymers. These fractions, F_1' and F_1'', were determined from 100 MHz ^{1}H n.m.r. spectra by comparing the areas of the phenyl proton

Table 1 Preparative and analytical data for ST–MVK copolymers used for the determination of reactivity ratios

Copolymer	ST, M_1 (g)	MVK, M_2 (g)	AIBN (g)	C_6H_6 (ml)	Time (h)	Conv. (%)	f_1	f_2	F_1^a	F_2^a
1	1.58	8.42	0.019	17	1	5.0	0.112	0.888	0.25(1)	0.74(9)
2	1.58	8.42	0.021	16	1	10.0	0.112	0.888	0.28(6)	0.71(4)
3	1.58	8.42	0.021	15	1	9.8	0.112	0.888	0.25(1)	0.74(9)
4	1.58	8.42	0.020	15	1	8.5	0.112	0.888	0.25(4)	0.74(6)
5	1.59	8.46	0.022	14	1	8.6	0.112	0.888	0.28(1)	0.71(9)
Average							0.112	0.888	0.265	0.735
6	8.70	1.30	0.022	15	1.5	3.5	0.819	0.181	0.72(1)	0.27(9)
7	8.70	1.30	0.021	15	1.5	6.9	0.819	0.181	0.74(2)	0.25(8)
8	8.70	1.30	0.029	15	1.5	7.6	0.819	0.181	0.70(6)	0.29(4)
9	8.75	1.31	0.026	15	1.5	5.5	0.818	0.182	0.72(0)	0.28(0)
10	8.74	1.30	0.024	15	1.5	4.5	0.819	0.181	0.73(8)	0.26(2)
Average							0.819	0.181	0.725	0.275

[a] Determined by ^{1}H n.m.r. spectroscopy (see text for details)

Table 2 Preparative and analytical data for ST–MVK copolymers used in photolysis experiments

Copol.	ST (g)	MVK (g)	AIBN (g)	C_6H_6 (ml)	Time (h)	Yield (%)	f_1(init)	f_1(final)	F_1(init)	F_1(final)	F_1(cum)^a
11	22.28	2.64	0.040	15	1.5	4.9	0.894	0.898	0.809	0.815	0.78
11a	22.28	2.64	0.041	15	1.5	4.0	0.894	0.897	0.809	0.814	0.77
11b	22.28	2.64	0.040	15	3.0	7.5	0.894	0.900	0.809	0.818	0.74
12	9.38	0.70	0.021	18	18	42	0.900	0.939	0.817	0.877	0.82
13	15.00	0.60	0.024	17	4.5	11.2	0.944	0.950	0.884	0.895	0.85

[a] Determined by n.m.r. analysis (see text for details)

peaks from the ST units with the total proton peak areas. The optimized feed fractions were calculated using the equations $f_1' = 2/(2 + r_1)$ and $f_1'' = r_2/(2 + r_2)$, with estimates of r_1 and r_2 of 0.444 and 0.252, respectively (obtained from the published Q and e values[17]: $Q_1 = 1.00$, $Q_2 = 0.68$, $e_1 = -0.80$, and $e_2 = 0.69$). The analytical data are given in *Table 1* (samples 1–10) and when used in the Mayo–Lewis (copolymer composition) equation[18] give $r_1 = 0.40$ and $r_2 = 0.24$ with 95% confidence. These reactivity ratios are somewhat different from those published by Lewis *et_al.*[19] (0.29 and 0.35, respectively) and are, we believe, more reliable given the optimized procedure by which they have been determined. They also differ significantly from the values that may be calculated using the recently revised Patterns scheme of Jenkins and Jenkins (0.58 and 0.32)[20]. In this instance, surprisingly, given the simple structures of the monomers involved, the Patterns scheme seems to be a less successful predictor of reactivity ratios than the older Q and e scheme.

With the aid of calculations based on the reactivity ratios, three more ST–MVK copolymers (one in triplicate) were prepared for photolysis experiments (samples 11–13). Details of these preparations are given in *Table 2*, which includes also the initial and final fractions of ST in the feed, f_1(init) and f_1(final), the initial and final fractions of ST units in the instantaneous copolymers produced at the outsets of the reactions and at the points of conversion at which the copolymerizations were terminated, F_1(init) and F_1(final), and the fractions of ST units in the recovered, cumulative copolymers, F_1(cum), determined by n.m.r. The calculated fractions are based on the measured reactivity ratios. It can be seen that for all three copolymers the agreement between the measured and calculated copolymer compositions is reasonable, and that for none of the copolymers has there been more than a small drift in composition with conversion (even in preparation 12 which was taken to 42% conversion). It may be assumed, therefore, that the copolymers are close to homogeneous with respect to both composition and monomer unit sequence distribution.

Table 3 gives number-average and weight-average lengths (P_nST, P_nMVK, P_wST and P_wMVK) and molar masses (M_nST, M_nMVK, M_wST and M_wMVK) for both ST and MVK monomer unit sequences in the copolymers. These quantities are averaged over all chains and also over the appropriate conversion intervals. The rationale behind these calculations has been given elsewhere[2]. From the data in *Table 3*, it can be seen that most of the MVK units in the copolymers are in isolated sequences (monads) whereas the ST units occur, on average, in runs of 4–9 (tetrads to nonads). Thus, scission of the copolymers adjacent to the MVK units would be expected to give ST oligomers containing, on average, 4–9 ST repeat units.

Photolyses of ST–MVK copolymers

Table 4 gives the results of the photolysis experiments. Included in *Table 4* are the number-average molecular

Table 3 Calculated number-average and weight-average lengths (P_n and P_w) and molecular weights (M_n and M_w) for ST and MVK sequences in ST–MVK copolymers

Copol.	P_nST	P_nMVK	P_wST	P_wMVK	M_nST	M_nMVK	M_wST	M_wMVK
11	4.45	1.03	7.88	1.06	463	72	821	74
11a	4.42	1.03	7.86	1.06	460	72	817	74
11b	4.48	1.03	7.97	1.06	466	72	829	74
12	5.67	1.03	10.34	1.05	581	72	1077	74
13	8.15	1.01	15.32	1.03	849	71	1596	72

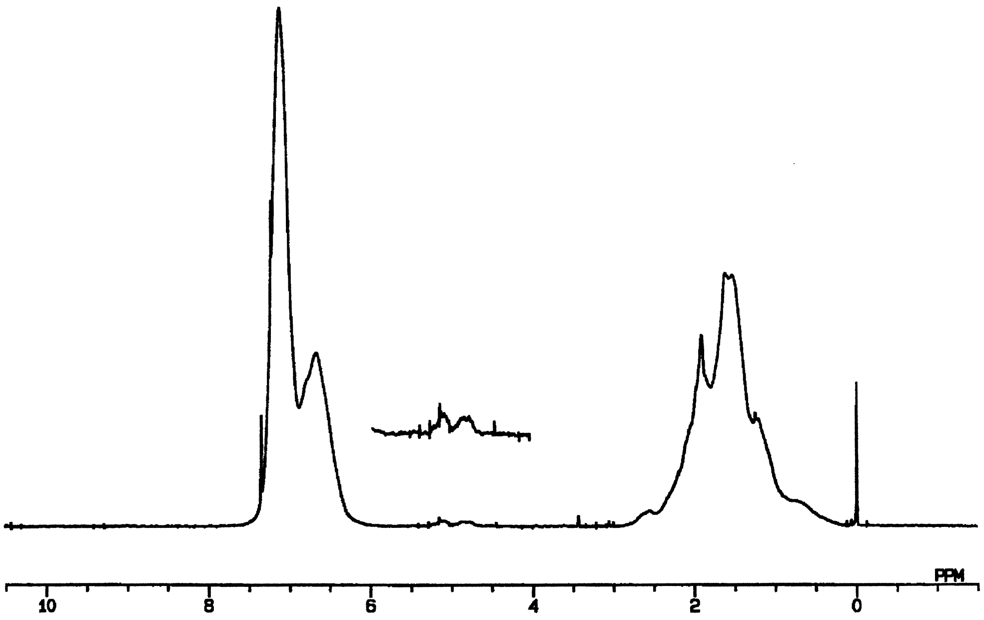


Figure 1 A ^{1}H n.m.r. spectrum of the oligomeric products from the photolysis of ST–MVK copolymer 11b (run 1b in *Table 4*) with a vertical expansion showing olefinic proton resonances at 4.7 and 5.2 ppm arising from unsaturated, styrenic end-groups.

Table 4 Experimental data and results for the photolyses of ST–MVK copolymers

Copol.	Run no.	Wt. polymer[a] (g)	Photolysis time (h)	M_n	M_w	D	s
11		–	0	86000	164000	1.9	0
	1	0.513	96[b]	2100	9400	4.5	40
11a		–	0	109800	199100	1.8	0
	1a	0.402	168	3400	8200	2.4	31
11b		–	0	113300	198600	1.8	0
	1b	0.401	168	3500	8800	2.5	31
Theoretical limits			–	460	820	1.8	186
12		–	0	71000	129000	1.8	0
	2	0.527	4	10000	39000	3.9	6
	3	0.524	4[c]	43000	100000	2.3	1
	4	0.524	24	1800	5500	3.1	38
	5	0.521	72	3100	12000	3.9	23
	6	1.98	90[b]	9500	30000	3.2	6
	7	0.530	168	1400	7000	5.0	50
Theoretical limits				590	1100	1.9	119
13		–	0	88000	154000	1.8	0
	8	0.534	312	2100	7400	3.5	41
Theoretical limits				850	1600	1.9	103

[a] All samples were dissolved in 25 ml of benzene

[b] Photolysis at 350 nm, remainder at 300 nm

[c] The photolysis was carried out in the presence of 0.24 g of added nitrosobenzene

weights, M_n, and dispersities, D, of the starting copolymers (determined by g.p.c.), molecular weights for the oligomers produced by photolysis, the average numbers of scissions per chain calculated from the molecular weights of the oligomers and those of the starting copolymers, and the theoretical limiting molecular weights, dispersities and numbers of scissions per chain calculated from the mean sequence lengths given in *Table 3*. It can be seen that all three copolymers (samples 11–13) are cleaved by u.v. light at 300 or 350 nm and that, as the time of photolysis is increased, the molecular weights of the oligomers formed decrease, as expected. However, even at long photolysis times, the theoretical limiting degrees of scission, s, are not reached. A similar effect was seen in photolyses of MMA–MVK copolymers[1,2]. Apparent incomplete chain scission may be a consequence either of radical coupling (cross-linking) reactions following competing Norrish type I processes or of radical polymerization of some of the unsaturated end-groups arising from the Norrish type II process. Repolymerization of end-groups has been suggested as being responsible for the decreased quantum yields for chain scission observed at high extents of photodegradation in poly(methyl vinyl ketone)[6]. It will be noticed that in one experiment in which nitrosobenzene, a radical trap, was added (*Table 4*, run 3), the degree of chain scission was much reduced compared with that in an identical experiment carried out without nitrosobenzene (run 2). This result would seem to confirm the biradical nature of the intermediate in the Norrish type II reaction.

Table 5 Calculated and measured molecular weights for ST oligomers from photolyses of ST–MVK copolymers

Photolysis	M_n(n.m.r.)[a]	M_n(g.p.c.)	M_n(theoret)[b]
Run 4	2200	1800	590
Run 5	3100	3100	590
Run 7	2000	1400	590
Run 8	1500	2100	850

[a] For method of determination, see text

[b] Calculated limiting molecular weights assuming complete scission of MVK units (see *Table 4*)

Figure 1 shows the ^1H n.m.r. spectrum of one of the oligomeric products of photolysis, that from run 1b (see *Table 4* for details), together with a vertical expansion of the region between 4 and 6 ppm. The signals between 1 and 3 ppm arise from the aliphatic protons of the styrene repeat units, whilst those between 6 and 7.5 ppm are from the aromatic protons of the repeat units. The region chosen for expansion is that expected to encompass the olefinic proton signals from unsaturated, styrenic end-groups. It can be seen that there are only two significant signals in this region and that both are multiplets. The multiplet at 4.7 ppm is assigned to H_a in the expected styrenic end-group (structure I in *Scheme 1* with $R = Ph$ and $R' = CH_3$) and that at 5.0 ppm to H_b. α-Methyl styrene, a model compound for this type of end-group, gives similar signals at 4.76 ppm and 5.05 ppm, respectively. All the other styrene oligomers produced by photolysis have ^1H n.m.r. spectra similar to that shown in *Figure 1*, differing only in the ratio of end-group to main-group signals. Integration of the end-group signals and comparison with those from the main chain, together with the assumption that there is, on average, only one styrenic end-group per oligomer molecule, allows M_n to be calculated. The M_n values determined from the ^1H n.m.r. spectra and by g.p.c. are compared in *Table 5*. It can be seen from this table that the agreement is generally good, confirming the presence, on average, of only one styrenic end-group per oligomer molecule. The presence of unsaturated styrenic end-groups in the oligomers is indicated also in the ^{13}C n.m.r. spectra which contain, in addition to the expected large aromatic signals from the ST repeat units at 125–129 ppm and 144–146 ppm, much smaller signals at 114 ppm (see *Figure 2*(*a*) for an example) which we attribute to the olefinic methylene carbon atom of the end-group. The olefinic methylene carbon atom signal in

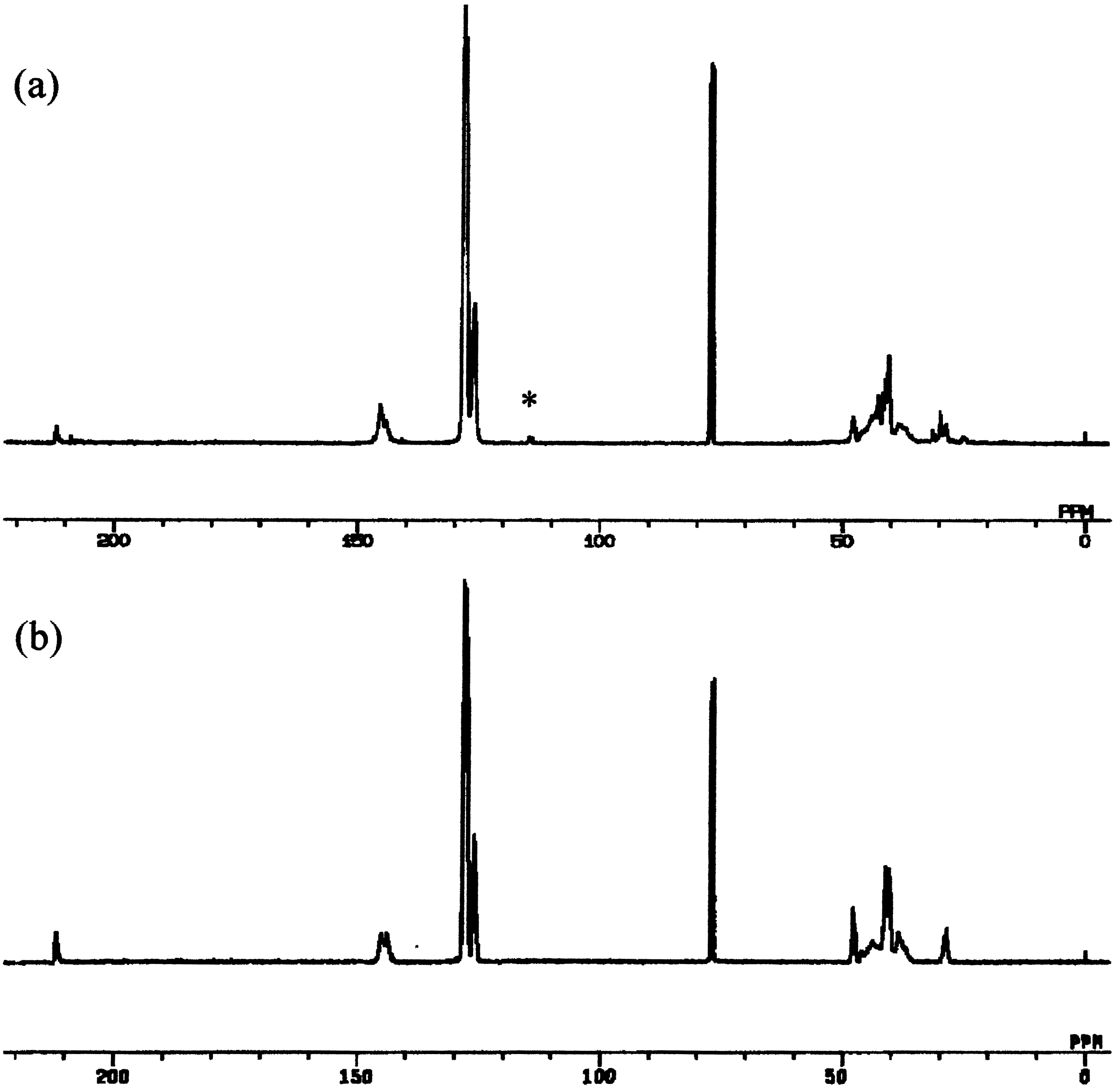
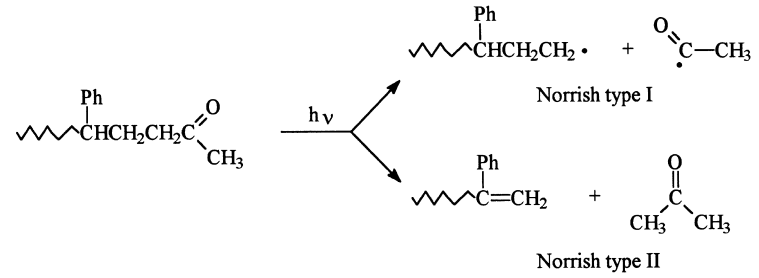


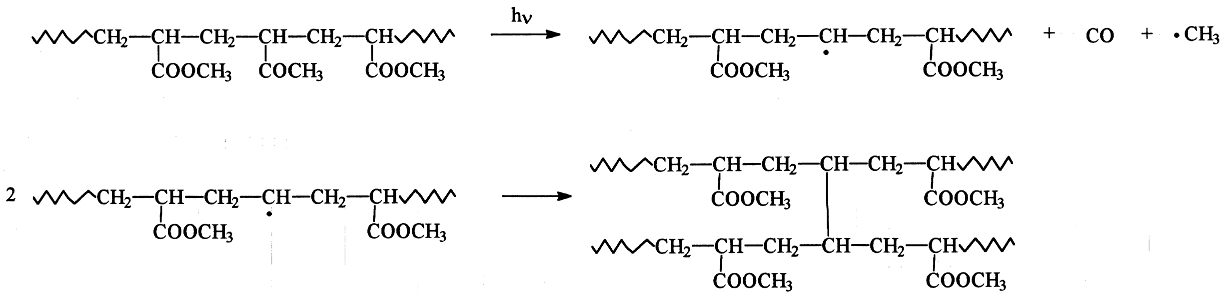
Figure 2 The ^{13}C n.m.r. spectra of (a) ST oligomer from run 1b with olefinic carbon atom signals from unsaturated end-groups marked (*), and (b) the parent ST–MVK copolymer (copolymer 11b) from which this oligomer was obtained by photolysis (see *Table 4*).



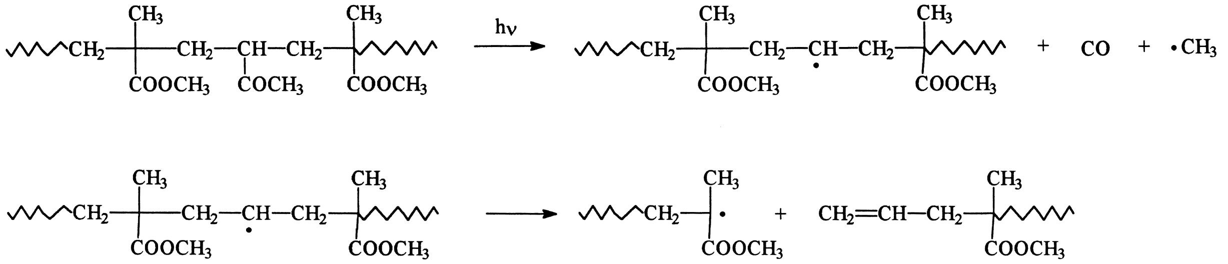
Scheme 2

α-methyl styrene, the model for this end-group, occurs at 111.5 ppm. The olefinic quaternary carbon atom of the end-group would be expected, by analogy with that in α-methyl styrene, to give a signal at 146 ppm; however, this region of the ^{13}C n.m.r. spectrum of the oligomer is occupied by signals from the aromatic carbon atoms of the ST repeat units, as indicated above. The olefinic methylene carbon atom signal is absent in the ^{13}C n.m.r. spectrum of the parent ST–MVK copolymer, as expected (see *Figure 2*(*b*)).

The other end-group on the oligomer would be expected to be a saturated ketone (structure II in *Scheme 1* with $R = Ph$ and $R' = CH_3$). However, such end groups can undergo further photolysis, by either a Norrish type I or a Norrish type II process (*Scheme 2*). Given the good agreement between the M_n values determined by n.m.r. and by g.p.c. (presented in *Table 5*), it seems most likely that the former reaction predominates giving, ultimately, saturated, non-carbonyl-group-containing end-groups. The



Scheme 3



Scheme 4

low concentration of carbonyl-group-containing end-groups has, in fact, been demonstrated by ^{13}C n.m.r. and by FT-i.r. spectroscopy. The carbonyl carbon atom signals at 212 ppm in the ^{13}C spectra of the oligomers obtained at long photolysis times are significantly smaller than those visible in the spectra of the parent copolymers (compare *Figure 2*(*a*) and 2(*b*), for example). Also, the ratio of carbonyl group absorbance (1710 cm^{-1}) to aromatic absorbance (1602 cm^{-1}) in the i.r. spectra of the oligomers (typically 0.6–1.2) is significantly lower than that for the corresponding absorbances in spectra of the parent copolymers (typically 2.1–2.7).

Photolysis of an MA–MVK copolymer

There is no *a priori* reason for supposing that photolyses of MA–MVK copolymers will differ significantly from those of ST–MVK, *i.e.* the major reaction is expected to be Norrish type II chain scission, leading to oligomeric fragments with methyl ketone and acrylic end groups (see *Scheme 1* and structures I and II with $R = COOCH_3$ and $R' = CH_3$). Indeed, it has already been reported that MA–MVK copolymers show high quantum yields for chain scission by what has been presumed to be a Norrish type II process[21]. However, to test this hypothesis, a single copolymer of MA and MVK was prepared by the free radical copolymerization of 16.87 g MA (mole fraction, 0.74) with 4.88 g MVK (mole fraction, 0.26) in 19 ml of benzene at 60°C under vacuum using AIBN (0.022 g) as initiator. The recovered yield of polymer after a 4.5 h polymerization was 13 g (61%). Analysis of this copolymer by ^{1}H n.m.r. spectrosopy (comparison of the area of the MA methoxyl group peaks with the total peak area) showed that it contained 0.81 mole fraction MA units and 0.19 mole fraction MVK units. The M_n and M_w for this copolymer, determined by g.p.c., were 330 000 and 644 000 (polystyrene equivalents), respectively. The polydispersity, D, was therefore 1.95.

Photolysis of this copolymer (0.556 g in 25 ml of benzene) under vacuum with light of wavelength 300 nm for 17 h gave an oligomeric product with $M_n = 2500$ and $M_w = 3\,900\,000$ (polystyrene equivalents), *i.e.* a product with an extremely broad molecular weight distribution ($D = 1600$!). This feature would seem to indicate that the copolymer undergoes both chain scission and cross-linking during photolysis, possibly as a consequence of combinations of main-chain radicals produced during a minor, competing, Norrish type I process (*Scheme 3*). Alternatively, unsaturated end-groups may be repolymerizing to a considerable extent during photolysis.

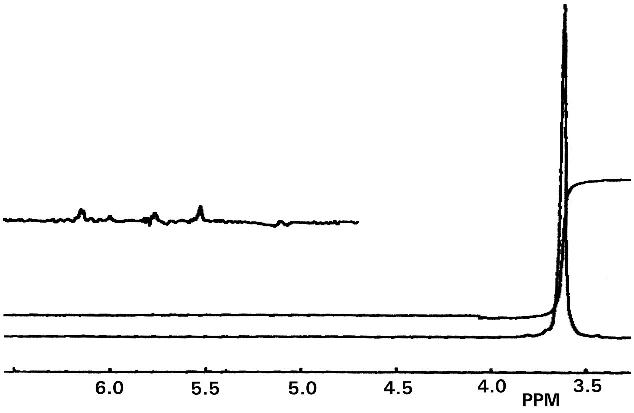


Figure 3 Part of the ^{1}H n.m.r. spectrum of the product from the photolysis of a MA–MVK copolymer with a vertical expansion showing olefinic proton resonances at 5.5 and 6.2 ppm arising from unsaturated, acrylic end-groups.

At first sight, it might be expected that a similar competition between chain scission and cross-linking/ repolymerization would have been observed in the predominantly Norrish type I photolysis of MMA–MVK copolymers[1,2]. However, in MMA–MVK the macroradical produced in the Norrish type I process, on further scission, can give a stable, tertiary radical (*Scheme 4*), whereas the same sequence following photolysis in MA–MVK would give a less stable, secondary radical, and is presumably therefore less probable. Also, the allylic end-groups produced in the photolysis of MMA–MVK copolymers are not readily polymerized.

The oligomeric products of the photolysis of the MA–MVK copolymer were examined by both ^{1}H and ^{13}C n.m.r. spectroscopy. The spectra were essentially characteristic of poly(methyl acrylate) but the ^{1}H spectrum (*Figure 3*) did indicate the presence of low concentrations of acrylic end-groups arising from Norrish type II chain scission, *i.e.* the spectra contained small signals at 5.5 ppm and 6.2 ppm arising from H_a and H_b, respectively, in structure 1 (see *Scheme 1*, with $R = COOCH_3$ and $R' = CH_3$).

Copolymerizations of ST oligomers

If the oligomers produced by the photolysis of ST–MVK copolymers have styrenic end-groups, as suggested above, then in theory they are polymerizable, *i.e.* the oligomers are

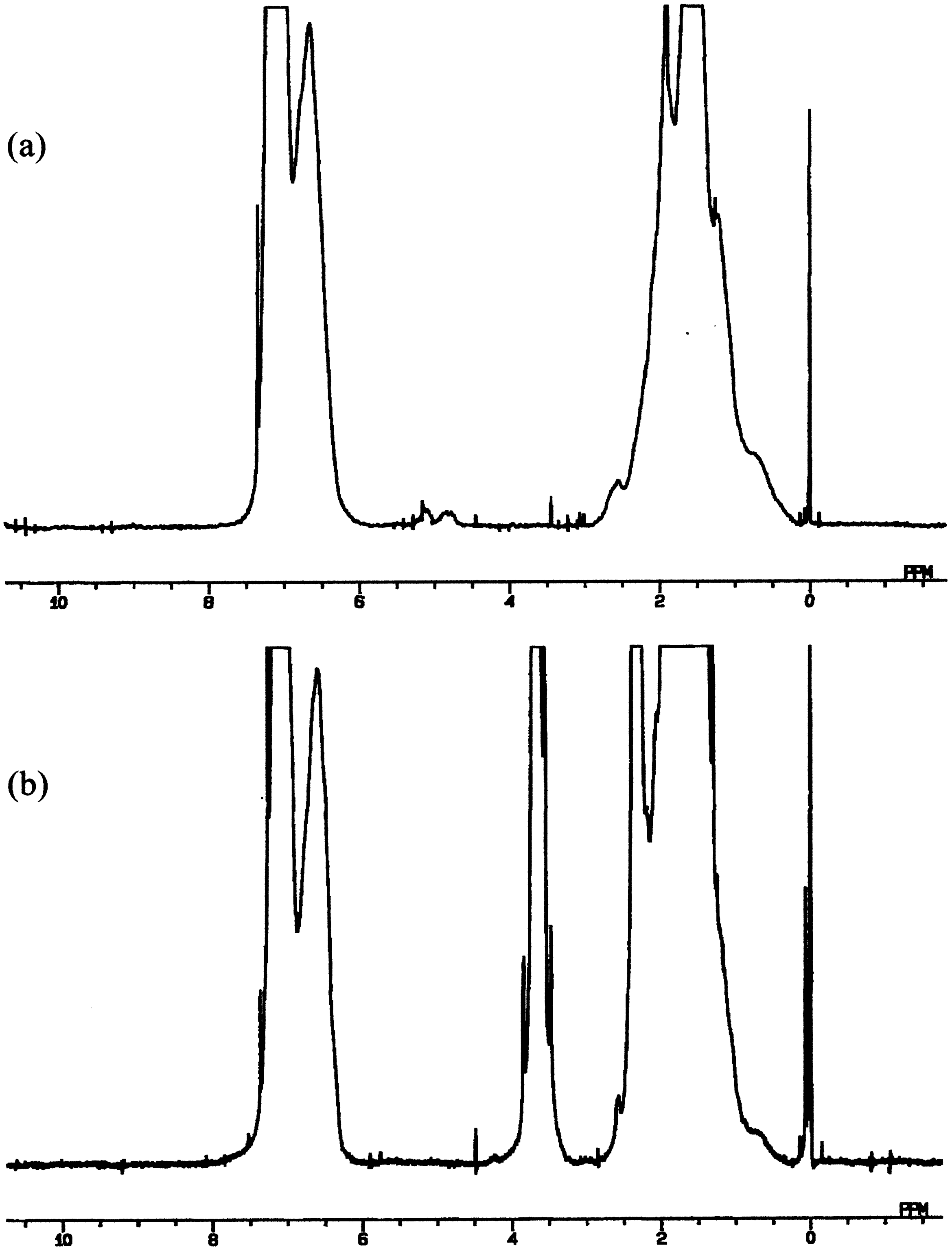


Figure 4 The ^{1}H n.m.r. spectra of (a) an oligomeric product from the photolysis of a ST–MVK copolymer (run 1b in *Table 4*), and (b) the polymeric product produced on copolymerizing this oligomer with MA for 48 h, showing loss of end-group signals following copolymerization (see *Table 6* for details of the experiment). The spectra have been scaled so that the ST aromatic signals at 6–7.5 ppm in both cases are of the same intensity.

Table 6 Yields and molecular weights of polymers obtained from polymerizations of ST oligomers with methyl acrylate (MA)

Source of oligomer	Wt. of ST oligomer used[b] (g)	MA (g)	AIBN (g)	Time (h)	Yield[a] (%)	M_n	M_w	D
Run 1a	0.1281	0.1600	0.004	24	51.4	8000	60300	7.5
Run 1b	0.1150	0.1576	0.004	48	57.0	7700	37100	4.8

[a] Based on weight of ST oligomer plus weight of MA
[b] Dissolved in 1.5 ml of benzene

macromonomers since they have end-groups analogous in structure to those of α-methyl styrene. However, α-methyl styrene cannot be homopolymerized by a radical mechanism, at least not at the temperatures used normally for such polymerizations (typically 50–90°C), owing to a low ceiling temperature[22]. For this reason, it seems unlikely that the styrenic-ended oligomers will therefore be easy to homopolymerize.

Nevertheless, α-methyl styrene can readily be free-radically copolymerized with electron-acceptor-type monomers such as maleic anhydride, methyl methacrylate and acrylonitrile[23–25]. Thus, we have attempted to copolymerize small quantities of the macromonomeric products obtained from photolyses of ST–MVK copolymers with methyl acrylate (MA), also an acceptor-type monomer, at 60°C in very small volumes of benzene under vacuum using azoisobutyronitrile (AIBN) as initiator. Two such copolymerizations were carried out, one for 24 h and one for 48 h. The polymeric products of these attempted copolymerizations were recovered by precipitation in methanol and were characterized by g.p.c. and by ^{1}H n.m.r. spectroscopy.

The results of these two copolymerizations are given in *Table 6*. In both cases, yields of low molecular weight polymer of just over 50% (w/w) were obtained, *i.e.* slightly more polymeric material was recovered than had been introduced originally in the form of ST oligomer. Also, the number-average molecular weights of these products are higher (by about a factor of two) than those of the starting oligomers and also the polydispersities have increased substantially. These data alone would seem to suggest that the ST oligomers have been incorporated into a polymer, albeit a polymer of low molecular weight. However, one cannot exclude, on the basis of these data alone, the possibility that what was recovered was a mixture of unchanged styrene oligomer (the putative macromonomer) and low molecular weight homopoly(methyl acrylate). That this is not the case is revealed by the ^{1}H n.m.r. spectra of the products (see *Figure 4*) which contain large signals characteristic of the aromatic protons of ST units (between 6 and 7.5 ppm) and of the methoxyl groups of incorporated MA units (at 3.7 ppm) but in which signals characteristic of the unsaturated end-groups in the original ST oligomers (around 4.7 and 5.0 ppm) are absent.

CONCLUSIONS

Styrene–methyl vinyl ketone copolymers, when photolyzed, undergo Norrish type II chain scission to give oligomers containing unsaturated end-groups having structures analogous to that of α-methyl styrene. These oligomers can be copolymerized free-radically with methyl acrylate (*i.e.* they behave as macromonomers) to give, presumably, comb-like copolymers.

Methyl acrylate–methyl vinyl ketone copolymers appear to undergo both chain scission and significant cross-linking or repolymerization when irradiated. Chain scission in these copolymers is confirmed also to be a Norrish type II process, giving rise to fragments with unsaturated end-groups of an acrylic type.

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