polymer papers

Photolysis of methyl methacrylate–methyl vinyl ketone copolymers. A new route to acrylic macromonomers?

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The u.v. photolysis of statistical methyl methacrylate–methyl vinyl ketone copolymers containing relatively small amounts of methyl vinyl ketone is shown, by n.m.r. and g.p.c. analysis, to give rise to oligo(methyl methacrylate)s with allylic end-groups that are not readily polymerizable. Thus it is concluded that the photolysis proceeds predominantly via a Norrish type I process rather than by a modified Norrish type II process as previously suggested. The Norrish type II process, however, is a minor contributor to the overall reaction and gives rise to some oligomeric fragments with acrylic end-groups.

(Keywords: methyl methacrylate; methyl vinyl ketone; copolymer)

INTRODUCTION

Reactive oligomers, such as terminally functionalized (telechelic) oligomers and macromonomers, are attracting increasing interest as intermediates for use in various types of reactive processing and in the synthesis of speciality block and graft copolymers. Telechelic oligomers are currently most often prepared by addition polymerization using functionalized initiators and/or functionalized terminating or transfer agents, or by low conversion step-wise (condensation and rearrangement) polymerization. Macromonomers may be prepared either by initiating or terminating an ionic polymerization with a reagent containing a post-polymerizable functional group or from telechelic oligomers by suitable further reaction.

We have been interested for some time in the synthesis of telechelic oligomers by a relatively little-exploited method involving controlled scission of high molecular weight copolymers, and have published several papers on this work[1–4]. Our interest in this method of synthesizing reactive oligomers has recently led us to speculate as to whether or not it would be possible to synthesize macromonomers by similar methods. In particular we noted work by Amerik and Guillet[5] in which it was proposed that methyl methacrylate–methyl vinyl ketone copolymers photodegrade by an unusual variant of the Norrish type II reaction, involving H-atom transfer from a position δ to the ketone carbonyl (*Scheme 1*). It will be noted that the products of this reaction, if the mechanism shown in *Scheme 1* is correct, are oligomers, each of which should possess at one end, on average, an acrylic group. Such oligomers should behave as macromonomers.

In this paper we describe the synthesis and u.v. photolysis of some copolymers of methyl methacrylate (MMA) with methyl vinyl ketone (MVK) and examine the products of photolysis, particularly with regard to end-group structures, by high field nuclear magnetic resonance (n.m.r.). The preliminary results of this work have already been communicated[6].

EXPERIMENTAL

Monomers

MVK (Aldrich, 99% pure inhibited with 0.1% acetic acid and 0.05% hydroquinone) and MMA (Aldrich, 99% pure, inhibited with 65 ppm hydroquinone monomethyl ether) were freed from inhibitors by fractional distillation under reduced pressure, and were then dried over molecular sieves (Linde type 4A) and stored at −30°C until required for use.

Preparation of homopolymers and statistical copolymers

Homopolymers and statistical copolymers of MMA and MVK were prepared by free radical polymerizations in benzene solutions in glass ampoules under vacuum at 60°C, using α,α'-azoisobutyronitrile (AIBN) (Fluka, >98% pure) as initiator. The polymers were recovered by precipitation in methanol and purified by reprecipitation from chloroform/methanol. The polymers were dried to constant weight in a vacuum oven before use.

U.v. photolysis of polymers

Polymer solutions for photolysis were introduced into 50 ml quartz glass ampoules and degassed in the usual way, using three or four freeze/pump/thaw cycles on a vacuum line. The ampoules were then sealed off under vacuum. The concentrations of the solutions used were typically 2% w/v. The solvents used in photolysis experiments were benzene (u.v. cut-off, 278 nm), toluene

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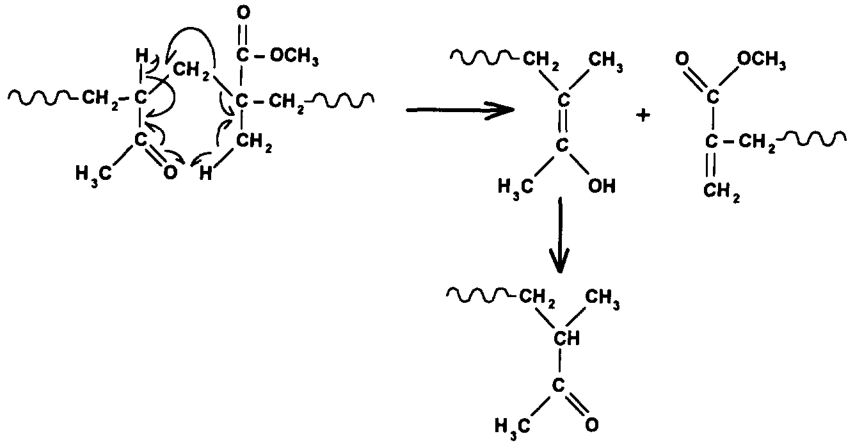


Scheme 1

(u.v. cut-off, 280 nm), ethanol (u.v. cut-off, 205 nm), methanol (u.v. cut-off, 205 nm) and tert-butyl alcohol (u.v. cut-off not determined), where cut-off is defined as the wavelength below which the transmittance falls below 10%.

Photolyses were carried out by mouting the degassed and sealed quartz ampoules (one at a time) at the centre of a Rayonet Photochemical Reactor containing 16 8 W u.v. lamps (Southern New England Ultraviolet Co.). Lamps were available having maximum intensities of emission at 350, 300 and 254 nm. During use, the ambient temperature at the centre of the photoreactor (not thermostatted) was about 60°C. The oligomeric products of photolysis were recovered by removal of the solvent on a rotary evaporator. In most cases, these products were purified by redissolution in chloroform and precipitation in methanol. Yields of oligomeric products of photolysis were generally better than 90% (based on weights of starting polymers).

Gel permeation chromatography

Gel permeation chromatography (g.p.c.) was used to determine molecular weights and molecular weight distributions of the homopolymers, copolymers and oligomers from the photolysis experiments. The g.p.c. system consisted of a Waters 510 solvent delivery pump, Rheodyne 7125 sample injection port, Waters 410 differential refractometer with three 10 cm Polymer Laboratories PLgel™ columns (10 μm particle size, mixed pore size) for the analysis of high molecular weight polymers, and two 10 cm Polymer Laboratories PLgel™ columns (5 μm particle size, 500 Å and 100 Å pore size) for the analysis of low molecular weight oligomers. Data were collected, stored and processed using a Polymer Laboratories GPC Data-station, Version 4.0. Typical operating conditions were: solvent, tetrahydrofuran (THF); flow rate, 1.0 ml min^{-1}; sample concentration, 0.25% w/v; injection volume, 20 μl; flow rate marker, toluene (h.p.l.c. grade). The columns were calibrated with three sets of Polymer Laboratories Easical™ monodisperse calibrants: high molecular weight polystyrenes; low molecular weight polystyrenes; and high molecular weight poly(methyl methacrylate)s.

Fourier transform infra-red spectroscopy

A Perkin Elmer 1720-X was used for Fourier transform infra-red spectroscopy (*FT*i.r.). Generally, spectra were the result of 20 scans with a resolution of 2 cm^{-1}. In all analyses, the background atmospheric spectrum was subtracted from the sample spectrum. Monomers were examined as liquid films sandwiched between pairs of KBr plates; polymer and oligomer samples were cast onto KBr plates from solutions in chloroform. The spectra were recorded and manipulated in absorbance mode.

Nuclear magnetic resonance spectroscopy

^{1}H n.m.r. spectroscopy at 60 MHz was used to check the purities of monomers and determine copolymer compositions. Spectra were recorded on 5% (w/v) solutions in $CDCl_3$ (Aldrich, 99.8 atom% D), with 1% (v/v) tetramethylsilane (TMS) as internal reference, using a Jeol JNM-PM X60SI continuous wave spectrometer.

High field n.m.r. was used for detailed analysis of polymer and oligomer structure. Most of the 400 MHz ^{1}H and 100 MHz ^{13}C n.m.r. spectra were recorded by the SERC high field n.m.r. service at the University of Warwick using a Bruker WH-400 *FT*n.m.r. spectrometer, although a few spectra were recorded on a Jeol JNM-GSX400 *FT*n.m.r. spectrometer at Lancaster. For ^{1}H n.m.r., typical operating parameters were: sweep width, 4032 Hz; pulse width, 4 μs; acquisition time, 4.1 s; number of scans, 32, 64 or 128. For ^{13}C n.m.r., typical operating parameters were: sweep width, 25 000 Hz; pulse width, 10 μs; acquisition time, 0.66 s; number of scans, ~40 000.

RESULTS AND DISCUSSION

Compositions and monomer sequence distributions of MMA–MVK copolymers

Reactivity ratios for the radical copolymerization of MMA (M_1) and MVK (M_2) in benzene at 60°C, initiated with AIBN, were determined using the protocol recommended by O'Driscoll and Reilly[7], 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 MMA units, F'_1 and F''_1, in the resulting copolymers. These fractions were determined from 60 MHz ^{1}H n.m.r. spectra by comparing the areas of the methoxyl proton resonances from the MMA units with the total proton peak areas. The optimized feed fractions were calculated using the equations, $f'_1 = 2/(2+r_1)$ and $f''_1 = r_2/(2+r_2)$, together with Grassie and Davidson's[8] values of r_1 and r_2 for this system, 0.63 and 0.53, respectively. The analytical data for these polymers are given in *Table 1*.

Use of the data in *Table 1* in the Mayo–Lewis (copolymer composition) equation[9] gives $r_1 = 1.10$ and $r_2 = 0.76$ with 95% confidence. With the aid of these reactivity ratios, three more MMA–MVK copolymers were synthesized for photolysis studies. Details of these syntheses are given in *Table 2*. *Table 2* also includes calculated initial and final fractions of MMA in the feed, f_1(inst), initial and final fractions of MMA units in the instantaneous copolymers being produced at the beginnings and ends of the reactions, F_1(inst), and the calculated and experimentally determined (by n.m.r.) fractions of MMA units in the final, cumulative, copolymers, F_1(cum). The calculated fractions are based upon the measured reactivity ratios. It can be seen that for all three copolymers (samples 11–13) 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. It may be assumed, therefore, that the copolymers are close to homogeneous with respect to both compositions and monomer unit sequence distributions.

Table 3 presents number-average and weight-average lengths ($P_{n\text{MMA}}$, $P_{n\text{MVK}}$, $P_{w\text{MMA}}$ and $P_{w\text{MVK}}$) and molar masses ($M_{n\text{MMA}}$, $M_{n\text{MVK}}$, $M_{w\text{MMA}}$ and $M_{w\text{MVK}}$) for both MMA and MVK sequences in the copolymers. These quantities are averaged not only over all chains but also over the appropriate conversion increments, taking into account the very slight changes in feed compositions with conversion. These calculations are of relevance when considering the likely sizes of MMA oligomers to be produced by photolysing the copolymers, if it is assumed that photolysis takes place only at MVK units. Details of the calculations are given in full elsewhere[10].

Also included in *Table 3* are number-average molecular weights, M_n, and polydispersities, D, for the copolymers determined by g.p.c. From the data in *Table 3* it can be seen that most of the MVK units in the copolymers are expected to be isolated (monads), with very few longer sequences of such units. The MMA units, on the other hand, are expected to occur in runs of significant length (about four in the copolymer containing least MMA and about 13 in that containing most). That this is indeed the case can be seen in 100 MHz ^{13}C n.m.r. spectra of the copolymers, which exhibit no visible signal at 48 ppm, characteristic of a β-methylene carbon at the centre of MVK–MVK dyads. There are, however, β-methylene signals visible at 52.5 ppm, characteristic of MMA-MVK dyads, and at 54.5 ppm, characteristic of MMA–MMA dyads.

Table 1 Analytical data for MMA–MVK copolymers used for the determination of reactivity ratios

Sample	MMA (g)	MVK (g)	AIBN (g)	Benzene (ml)	Time (h)	Conv. (%)	f_1	F_1
1	1.84	4.90	0.020	28	1	6.7	0.208	0.248
2	1.84	4.90	0.009	29	1.5	7.3	0.208	0.225
3	1.85	4.92	0.011	28	1.5	8.8	0.209	0.240
4	1.85	4.90	0.011	29	1.5	7.7	0.209	0.254
5	5.55	14.65	0.024	18	1	7.7	0.210	0.280
Average							0.209	0.249
6	16.60	3.61	0.025	19	1	7.4	0.763	0.796
7	16.78	3.65	0.023	19	1	8.6	0.763	0.787
8	16.61	3.61	0.023	17	1	7.0	0.763	0.822
9	16.61	3.61	0.021	18	1	8.7	0.763	0.751
10	17.03	3.67	0.024	18	1	9.6	0.764	0.775
Average							0.763	0.786

Table 2 Analytical data for MMA–MVK copolymers used for photolysis studies

Sample	MMA (g)	MVK (g)	AIBN (g)	Benzene (ml)	Time (h)	Conv. (%)	f_1 (inst)[a]		F_1 (inst)[a]		F_1 (cum)[a]	
							initial	final	initial	final	calc.	n.m.r.
11	20.06	1.20	0.036	22	7	52	0.921	0.915	0.928	0.923	0.926	0.968
12	20.11	2.47	0.033	20	6	74	0.851	0.838	0.865	0.846	0.858	0.844
13	20.04	4.99	0.032	20	3.5	28	0.737	0.728	0.762	0.754	0.759	0.762

[a] See text for definitions of these quantities

Table 3 Calculated mean lengths and mean molar masses of MMA and MVK sequences, and overall number-average molecular weights and polydispersities, for MMA–MVK copolymers used in the photolysis studies

Sample	$P_{n\text{MMA}}$	$P_{w\text{MMA}}$	$M_{n\text{MMA}}$	$M_{w\text{MMA}}$	$P_{n\text{MVK}}$	$P_{w\text{MVK}}$	$M_{n\text{MVK}}$	$M_{w\text{MVK}}$	M_n	D
11	13.32	25.64	1334	2567	1.07	1.14	75	80	190 000	2.21
12	6.81	12.61	682	1263	1.15	1.29	80	91	268 000	1.94
13	4.01	7.02	401	703	1.28	1.56	90	109	147 000	1.77

Table 4 Results of photolyses of MMA–MVK copolymers. All photolyses carried out on solutions in 25 ml benzene under vacuum unless otherwise indicated

Run no.	Weight of polymer (g)	Wavelength (nm)	Photolysis time (h)	M_n (g.p.c.)	D (g.p.c.)	S
Sample 11						
Start				190 000	2.2	0
1	0.506	350	2	31 000	1.7	5
2	0.505	350	2	39 000	1.8	4
3	0.510	350	7	15 000	1.7	12
4	0.511	350	36	2400	2.3	78
5	0.511	350	72	1500	1.6	126
Theoretical limit				1334	1.9	141
Sample 12						
Start				268 000	1.9	0
6	0.509	350	36	1400	2.4	190
7	0.505	350	42	1100	1.8	243
8[a]	0.506	350	42	1300	1.6	205
9[b]	0.555	350	62	1200	1.7	222
10	0.507	350	72	900	1.8	297
11	0.527	350	90	1500	1.5	178
12[c]	2.304	350	90	1500	1.7	178
13	0.527	350	132	1300	1.8	205
14[d]	0.495	350	140	1700	1.3	157
15	0.519	300	4	23 000	1.7	11
16[e]	0.519	300	4	72 000	1.8	3
17	0.540	300	16	1800	1.7	148
18	0.532	300	20	1700	1.6	157
Theoretical limit				682	1.9	392
Sample 13						
Start				147 000	1.7	0
19	0.515	350	92	550	2.7	266
20[f]	0.300	350	120	800	1.6	183
21	0.509	350	185	990	1.7	147
22	0.513	300	8	1300	2.0	113
23	0.537	300	24	720	2.4	203
24[g]	1.57	300	40	2300	2.3	63
Theoretical limit				401	1.8	366

[a] 25 ml benzene + 1.5 ml ethanol
[b] 25 ml benzene + 1.5 ml methanol
[c] 30 ml benzene
[d] 25 ml toluene
[e] 25 ml benzene + 0.24 g nitrosobenzene
[f] 20 ml benzene + 5 ml tert-butyl alcohol
[g] 40 ml benzene, photolysis carried out in air

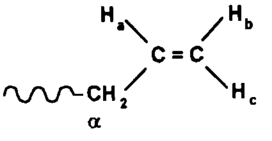
Photolyses of MMA–MVK copolymers

Samples of the three copolymers for which characterization data are given in *Tables 2* and *3* were photolysed in benzene solution for periods of up to 185 h using light of wavelengths 300 and 350 nm. Results from the photolyses are given in *Table 4*. S in *Table 4* is the calculated average number of scissions per chain and is obtained by dividing the initial M_n of the copolymer by M_n of the oligomer obtained from it on photolysis, and subtracting one. The theoretical limits to M_n, D and S given in the table are calculated assuming that the limiting molecular weight of the oligomer is determined by complete photolysis of all the MVK units, leaving only sequences of MMA units. It should be noted that these calculations make no allowance for the end-groups of the oligomers so-formed, and are based simply upon summation of the molar masses of the appropriate number of MMA units. We are confident that MMA sequences are not photolysed in our experiments, since the molecular weight of a sample of poly(methyl methacrylate) (PMMA) was found to be little affected by irradiation of the polymer in benzene solution with light of wavelength 350 or 300 nm for periods of up to 50 h. On the other hand, irradiation of PMMA in benzene solution with light of 254 nm wavelength for 6 h led to substantial degradation (M_n reduced from 145 000 to 3300). That MVK sequences are degraded much more readily than MMA sequences was also confirmed by photolysing samples of poly(methyl vinyl ketone) (PMVK). For example, exposure of a solution of PMVK in benzene to light of wavelength 300 nm for only 6 h led to a more than 10-fold reduction in M_n (71 000 to 6000).

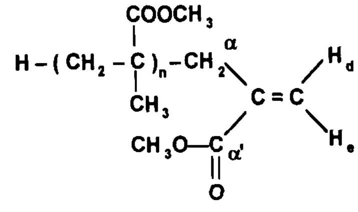
Table 4 reveals that increasing the time of photolysis in general increases the number of chain scissions, as expected[5], and that at long photolysis times, the molecular weights of the oligomers produced approach, but do not exactly match, the predicted limiting molecular weights. In fact, the use of extended photolysis times (e.g. runs 13, 14, 20 and 21) tends to lead to a small regrowth in molecular weight, possibly as a result of some crosslinking. Significant crosslinking is possibly also the reason for the unexpectedly high molecular weight of the oligomers produced in run 24, in which photolysis was carried out in the presence of air.

Examination of oligomers by n.m.r.

Spectra from 400 MHz ^{1}H n.m.r. and 100 MHz ^{13}C n.m.r. were recorded on most of the oligomeric products produced in the photolysis experiments. A typical ^{1}H n.m.r. spectrum, that for the oligomer produced in run 19, is shown in *Figure 1*. In many respects, the spectrum resembles that of PMMA, with few signs of any signals from MVK units, showing that, as expected, the MVK units have been extensively photolysed. The peaks at 0.8–1.2 ppm can be assigned to the α-CH_3 protons of MMA units, those at 1.8–2.2 ppm to the β-CH_2 protons of such units and that at 3.6 ppm to $-OCH_3$ protons. Of particular interest are very small olefinic proton signals at 5.1 and 5.6 ppm from unsaturated end-groups in the oligomers which, at first sight, seem to support the mechanism of photolysis for these copolymers proposed by Amerik and Guillet[5]. However, expansion of the region from 4.9 to 6.4 ppm (*Figure 2*) shows the pattern of resonances to be typical of an allylic end-group (**I**) rather than of an acrylic end-group (**II**), with $H_a = 5.70$ ppm, $H_b = 4.97$ ppm, $H_c = 5.03$ ppm and $(H_b + H_c)/H_a = 2$.



I



II

Also shown in *Figure 2* is the olefinic region of the ^{1}H n.m.r. spectrum of a genuine acrylic-ended MMA oligomer ($M_n = 5000$) made by the radical polymerization of MMA in the presence of cobaloxime, a catalytic chain transfer agent[11,12]. The pattern of olefinic peaks in the spectrum of the acrylic-ended material ($H_d = 5.5$ ppm, $H_e = 6.2$ ppm and $H_d/H_e = 1$) is seen to be quite different from that of the oligomer produced by photolysis. The different unsaturated end-group structures in the two types of oligomer can also be seen in ^{13}C n.m.r. spectra. *Figure 3* shows expansions of the carbonyl and olefinic carbon regions for the two oligomers. The spectrum of the genuine acrylic-ended oligomer contains signals from an olefinic methylene carbon at 128 ppm, from an olefinic quaternary carbon at 137 ppm, and from the carbonyl of the end-group (marked α' in **II**) at 168 ppm. However, the spectrum of the oligomer produced by photolysis shows two very different signals at 118 and 133 ppm, characteristic of the olefinic methine and olefinic methylene carbons of the allylic end-groups, respectively. Further evidence for the allylic end-group is a small signal at 51.5 ppm which appears as a shoulder on the MMA methoxyl carbon signal at 51.7 ppm and which may be assigned to the α-CH_2 carbon of the allylic group (marked α in **I**). As can be seen from *Figure 4*, this small signal grows in size relative to the methoxyl signal as the

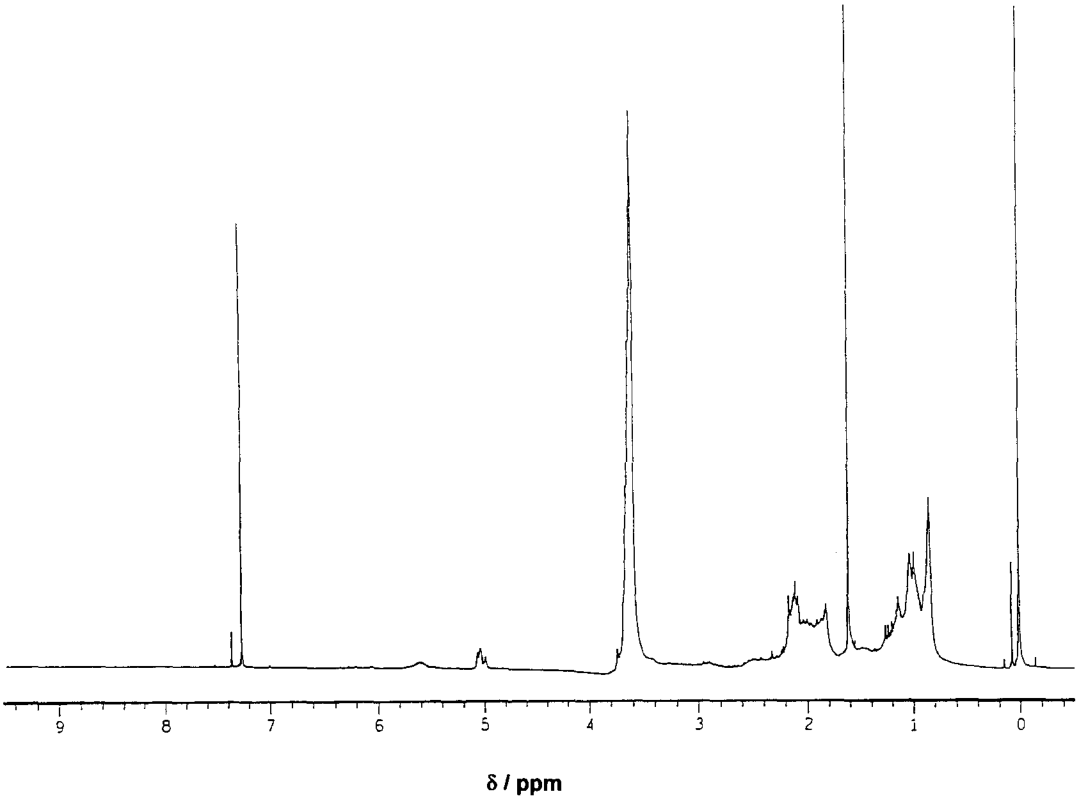


Figure 1 ^{1}H n.m.r. spectrum of MMA oligomer produced in run 19 (see *Table 4* for details)

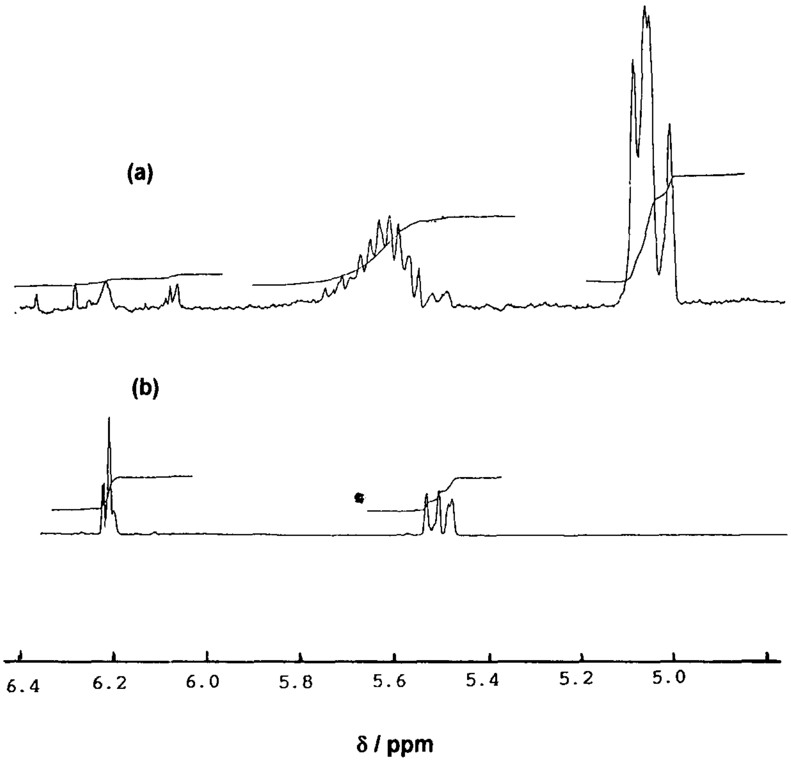


Figure 2 Signals from unsaturated end-groups in ^{1}H n.m.r. spectra of (a) MMA oligomer produced in run 19 and (b) genuine acrylic-ended MMA oligomer

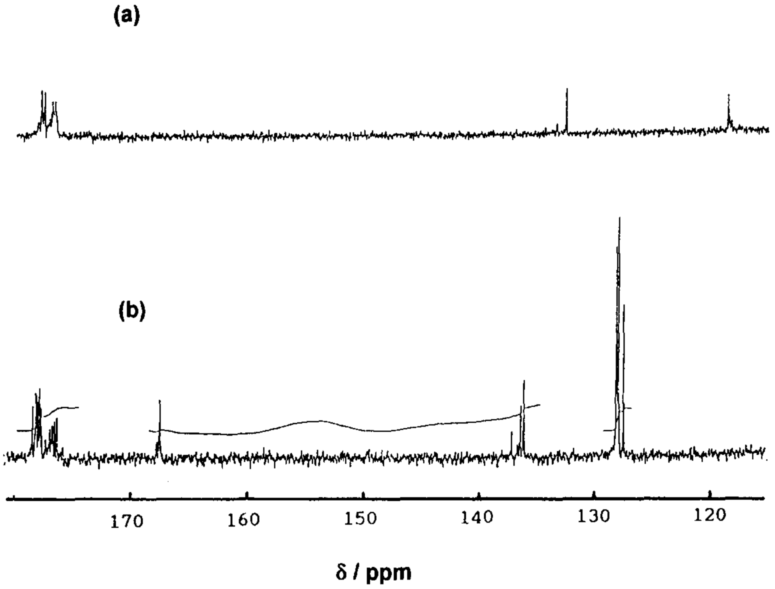


Figure 3 Expansions of olefinic and carbonyl carbon regions of ^{13}C n.m.r. spectra of (a) MMA oligomer produced in run 19 and (b) genuine acrylic-ended MMA oligomer

oligomer molecular weight is reduced, as expected for an end-group signal.

It appears on the basis of the n.m.r. evidence, therefore, that MMA-MVK copolymers photodegrade to give allylic-ended oligomers and not acrylic-ended oligomers as would be expected on the basis of the modified Norrish type II mechanism put forward by Amerik and Guillet[5]. However, before this mechanism can be rejected, it is necessary to show that acrylic-ended oligomers are not precursors to allylic-ended oligomers in a two-step photolysis. That this is not the case has been demonstrated by irradiating a benzene solution (0.545 g in 20 ml) of the genuine acrylic-ended MMA oligomer with light of wavelength 300 nm for 18 h. The molecular weight of the oligomer after irradiation was found not to have changed and the ^{1}H and ^{13}C n.m.r. spectra taken before and after irradiation were identical in every respect.

That photodegradation takes place exclusively at the MVK units is shown not only by the limiting molecular weight behaviour, apparent in the data presented in *Table 4*, but also by the almost complete absence of ketone carbonyl signals in the ^{13}C n.m.r. spectra of the oligomers.

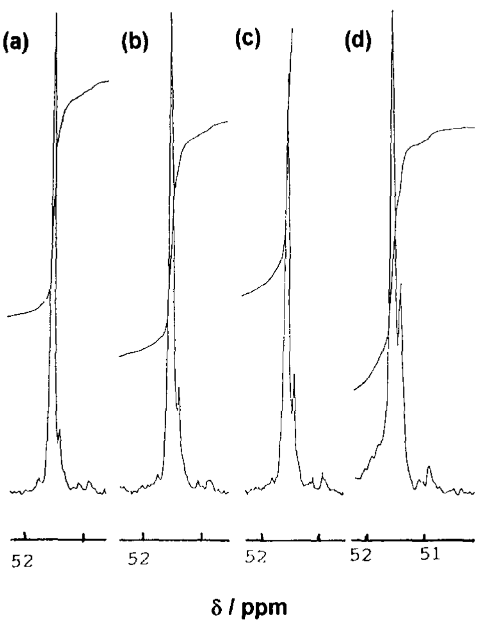


Figure 4 Part ^{13}C n.m.r. spectra of MMA oligomers of $M_n = 2400$ (a), 1400 (b), 900 (c) and 720 (d), produced in runs 4, 7, 10 and 24, respectively (see *Table 4* for details), showing increasing size of end-group CH_2 signal at 51.5 ppm relative to main-chain methoxyl signal at 51.7 ppm

Such signals are clearly visible, however, in the ^{13}C n.m.r. spectra of the parent copolymers, at 209 ppm.

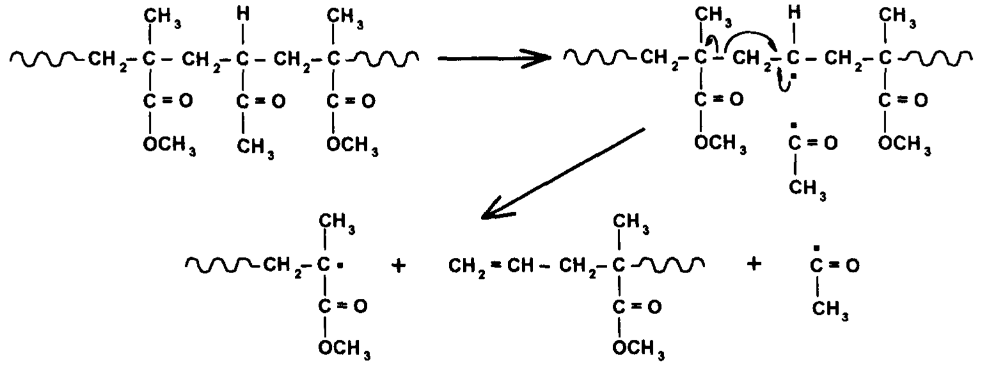
Mechanism of photolysis of MMA–MVK copolymers

It is clear from the results described above that the photolysis of MMA–MVK copolymers does not proceed by a modified Norrish type II mechanism as proposed by Amerik and Guillet[5], confirming doubts about this mechanism first expressed by Kato and co-workers[13,14]. Instead, we believe that MMA–MVK copolymers photodegrade by a Norrish type I process, in which excitation of the ketone carbonyl is followed by α-cleavage and this in turn is followed by chain scission β to the ketone unit (see *Scheme 2*). This mechanism is in essence identical to those proposed by others for the photolyses of poly(methyl isopropenyl ketone)[15], polymethacrylophenone[16,17], and copolymers of MMA with methyl isopropenyl ketone (MIPK)[18] and methacrylophenone (MAP)[16,19]; in all of these systems, as in MMA–MVK, there are no H atoms positioned γ to the ketone carbonyl and therefore available for transfer in a classic Norrish type II process.

However, the MMA–MVK system differs from the other copolymer systems mentioned above in one important respect, that is in the nature of the main chain radical formed by α-cleavage. In the cases of MMA–MIPK and MMA–MAP, α-cleavage leads to the formation of a stable tertiary radical on the main chain, whereas in MMA–MVK it leads to a less stable secondary radical. Nevertheless, there is a polymeric precedent for a Norrish type I reaction leading to a polymeric secondary radical followed by β-scission, and that is the photolysis of poly(tert-butyl vinyl ketone)[20–22]. Here, despite the presence of transferable γ H atoms, the major route to chain scission appears to be via a Norrish type I process, forming, in the first instance, a secondary polymer radical. It was suggested that the Norrish type I process was favoured over the Norrish type II process in this case because the type I process led to the production, from the side-chain, of a stable small radical, namely the tert-butyl radical. However, this is not the case here and, as far as we are aware, MMA–MVK photolysis is the first recorded instance of a polymeric ketone degrading by a Norrish type I process with the formation of neither a stable polymeric tertiary radical nor a stable small alkyl radical in the initial α-cleavage.

Although MMA–MVK copolymers appear to photodegrade almost exclusively by a Norrish type I mechanism, the occurrence of some degradation by the modified Norrish type II mechanism of Amerik and Guillet cannot be excluded. Careful examination of the ^1H n.m.r. spectra of the oligomeric products of photolysis reveals very small signals characteristic of acrylic end-groups at 5.5 at 6.2 ppm (see *Figure 3*). However, integration of these signals and comparison of their areas with those of the much larger signals from the allylic end-groups indicates that in no case does the concentration of acrylic end-groups exceed 8% of the concentration of allylic end-groups. The acrylic end-groups also contribute a very small signal at 3.7 ppm in the ^1H n.m.r. spectra of the oligomers; this arises from the methoxyl protons of the terminal ester group (α′ substituent in **II**).

The effect of polar solvents, such as alcohols, upon the efficiency of the Norrish type II reaction has been well documented in studies on low molecular weight ketones[23,24]. For example, the addition of 20% (v/v) tert-butyl alcohol was found to increase the quantum yield for the Norrish type II process in valerophenone from 0.40 to 0.85 in a non-polar solvent[23]. It has been proposed that the biradical intermediate formed on

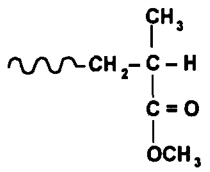


Scheme 2

excitation of the ketone hydrogen bonds to the hydroxyl group of the alcohol, thus hindering return to the starting ketone. It seems reasonable that such an effect might occur in the photolysis of MMA–MVK copolymers and thus might be exploited to increase the efficiency of the clearly unfavourable Norrish type II process. However, three photolyses in which an alcohol was added to the reaction mixture (runs 8, 9 and 20) gave no significant increase in the concentration of acrylic end-groups in the resulting oligomers relative to allylic end-groups. This failure to promote the Norrish type II reaction may be a result of the polymeric environment; similar failures to promote a type II process using alcohols have been reported for polyacrylophenone[25,26] and styrene–acrylophenone copolymers[27].

Attempts were also made to alter the balance between the Norrish type I and type II processes by suppressing the type I process through use of a radical scavenger. However, although addition of 1% (w/v) nitrosobenzene to a photolysis was found to reduce the extent of chain scission by almost 70% (cf. runs 15 and 16), there appeared, once again, to be little effect on the balance of the end-groups. Neither did the use of toluene as solvent, a more efficient H atom donor than benzene, influence in any significant way the degree of chain scission (cf. runs 13 and 14) nor the ratio of acrylic to allylic end-groups.

The type I photodegradation process (*Scheme 2*) should give rise not only to allylic end-groups but also to end-groups that are initially tertiary radicals. It seems highly likely, however, that these tertiary radicals will abstract H atoms, probably mainly from the solvent, and will therefore appear in the final products as methyl 2-methylpropanoyl end-groups (**III**). That this may be so is indicated by the appearance in the ^{1}H n.m.r. spectra of the oligomers of a sharp methyl proton peak at 1.15 ppm and a broad methine proton peak centred at about 2.4 ppm (see *Figure 1*). These peaks are in the same positions as the peaks from the equivalent 2-methyl and methine protons in a ^{1}H n.m.r. spectrum of methyl 2-methylbutanoate, a model compound for the saturated end-group.



$$\sim\!\sim\!\sim CH_2-\overset{\displaystyle CH_3}{\underset{\underset{\displaystyle OCH_3}{\displaystyle C=O}}{C}}-H$$

III

If the oligomers produced by photolysis of MMA–MVK copolymers have, on average, one allylic and one saturated end-group per chain, M_n values determined using a count of the end-groups should correspond with those determined by g.p.c. M_n values for various oligomers produced by photolysis have been calculated by comparing the area (A) of the ^{1}H n.m.r. signals from the allylic end-group at around 5 ppm (H_a and H_b in **I**) to the area (B) of the methoxyl proton signals at 3.6 ppm using the equation

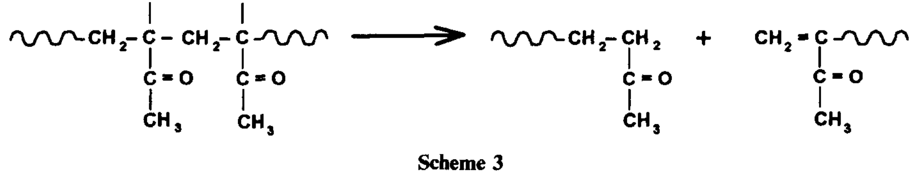
$$M_n=\left(\frac{B/3}{A/2}\times 100.12\right)+28$$

The constant, 28, represents the contribution to M_n of the mass of the methine proton of the saturated end-group and of the mass of the $CH_2{=}CH-$ fragment of the allylic end-group. The calculations do not take into account the low concentrations of acrylic end-groups. The results of these calculations are shown alongside those from g.p.c. in *Table 5*. It can be seen that in most cases the agreement between the M_n values calculated by the two methods is reasonable and would seem to confirm that the oligomers have, on average, one allylic end-group per chain.

The fact that the limiting M_n values for the oligomers are in all cases greater than those calculated assuming scission of all MVK units, is possibly an indication that whilst the α-cleavage occurs with 100% efficiency, the subsequent β-scission of the main chain does not. The question also arises as to what takes place within the dyad and longer sequences of MVK units in the copolymers. Although such sequences are few in number they may be expected to contribute some end-groups to the oligomers, especially those produced from sample 13, which is richest in MVK (and in which $P_{n\mathrm{MVK}}=1.28$, see *Table 3*). Longer sequences of MVK units would be expected to undergo photodegradation by both Norrish type I and type II processes, as does PMVK itself[28,29], since they possess available γ hydrogens. The Norrish type II process will give rise to both saturated and unsaturated ketone end-groups (*Scheme 3*). In ^{1}H n.m.r.

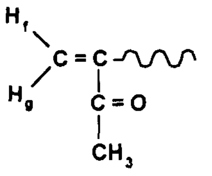
Table 5 Comparison of M_n values for oligomeric products of photolysis determined by ^{1}H n.m.r. end-group analysis with those determined by g.p.c.

Run no.	M_n by ^{1}H n.m.r.	M_n by g.p.c.
Sample 11		
4	2600	2400
5	2600	1500
Sample 12		
6	2100	1400
9	1500	1200
10	1800	900
11	1600	1500
13	1600	1300
17	1900	1800
18	1600	1700
Sample 13		
19	1800	550
21	1500	990
22	1600	1300
23	1400	720
24	2600	2300



Scheme 3

spectra of several of the oligomers, especially that produced from sample 13 in run 19, very small signals are visible at 6.25 and 6.05 ppm. We assign these to H_f and H_g, respectively, of the unsaturated ketone end-group, IV, produced by the type II process. The predicted chemical shifts for these two protons (approximating the attached MMA chain to an alkyl chain) are 6.09 and 5.90 ppm, respectively[30].



IV

Polymerizability of oligomers

Although the oligomers produced by the photolysis of MMA–MVK copolymers do not have predominantly acrylic end-groups as hoped, and therefore cannot be expected to be intrinsically polymerizable, at least not by a radical process, it was decided nevertheless to attempt to polymerize them. Accordingly, 0.17 g of the oligomeric product produced in run 22 (*Table 4*) was dissolved in benzene (2 ml) and sealed under vacuum with 0.0017 g AIBN. After heating for 17 h at 60°C, the mixture was poured into methanol and the precipitated product recovered and characterized by n.m.r. and g.p.c. It was found that the product was unchanged oligomer.

In a second experiment, 0.1 g of the same oligomeric product was mixed with ethyl acrylate (1.1 g) and AIBN

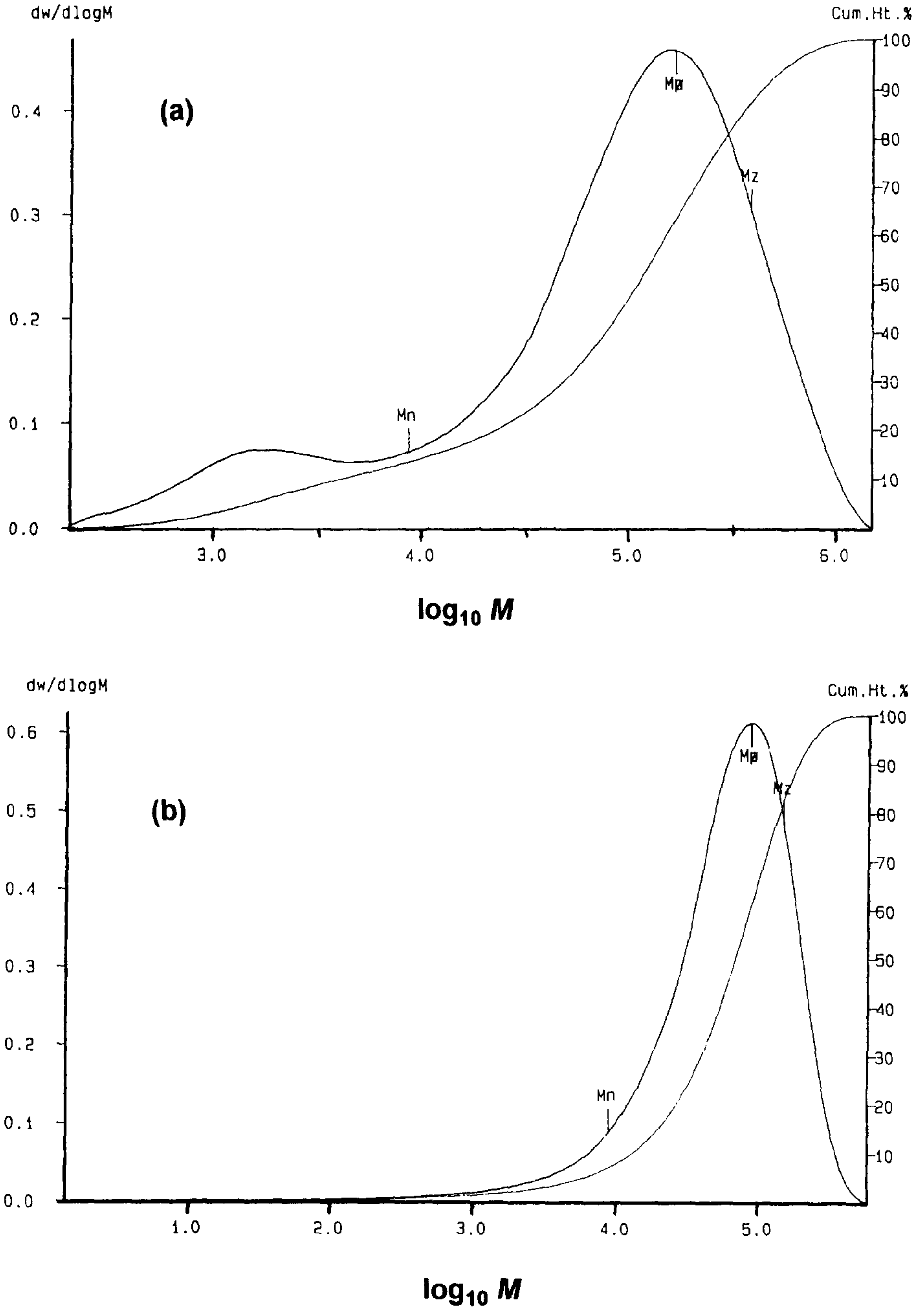


Figure 5 G.p.c. traces of (a) product from attempted copolymerization of MMA oligomer from run 22 with methyl acrylate and (b) product from successful copolymerization of genuine acrylic-ended MMA oligomer with methyl acrylate (see text for details)

(0.018 g) in benzene (5 ml) and again heated under vacuum at 60°C for 17 h. Recovery of the polymer and analysis by g.p.c. (*Figure 5a*) revealed it to be a mixture of poly(ethyl acrylate) with a peak molecular weight (M_p) of 1.6×10^5 and unchanged oligomer with $M_p = 1.7 \times 10^3$. However, under the same conditions, 0.124 g of a genuine acrylic-ended MMA macromonomer ($M_n = 5000$) mixed with 1.24 g ethyl acrylate and 0.018 g AIBN in 5 ml of benzene gave a homogeneous product with $M_p = 8.6 \times 10^4$ (*Figure 5b*). We conclude, therefore, that the allylic-ended MMA oligomers are not readily polymerizable, as expected, unlike the genuine acrylic-ended MMA macromonomer.

CONCLUSIONS

MMA–MVK copolymers photodegrade almost exclusively by a Norrish type I process, giving allylic-ended oligomers, and not by a modified Norrish type II process as proposed by Amerik and Guillet, although the type II process does appear to be a minor component of the overall reaction. The relative contributions of the predominant Norrish type I process and the minor modified Norrish type II process are not significantly dependent upon photolysis conditions. The oligomers formed by photolysis do not undergo radical homo- or copolymerization and are not therefore macromonomeric in the accepted sense. They could, however, conceivably be further functionalized to give macromonomers or be used as telechelics. The possibility still exists, however, that photolyses of other copolymers containing vinyl ketone units might produce polymerizable oligomers. We shall be reporting in due course on some studies of the photolyses of copolymers of MMA with methyl isopropenyl ketone, acrylophenone, *p*-chloroacrylophenone (PCAP) and *p*-tert-butylacrylophenone, of styrene with MVK and PCAP, and of methyl acrylate with MVK.

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