Photolysis of vinyl ketone copolymers: 3. Norrish Type I *versus* modified Norrish Type 2 chain scission in some methyl methacrylate–aryl vinyl ketone copolymers*

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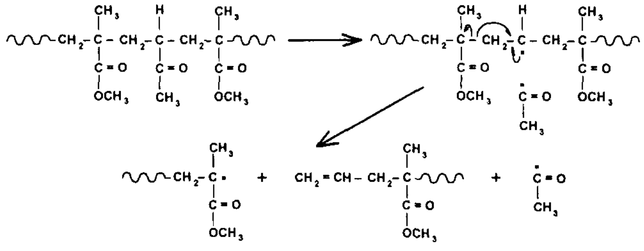
Copolymers of methyl methacrylate with acrylophenone, tert-butyl acrylophenone and *p*-chloroacrylophenone have been photolysed in benzene solution and the structures of the unsaturated end groups in the oligomeric products determined by n.m.r. It is shown that photodegradation takes place mainly by a Norrish Type I process, similar to that which occurs with methyl methacrylate–methyl vinyl ketone copolymers, but that there is a minor, non-classical Type II component which is most apparent in methyl methacrylate–*p*-butylacrylophenone.

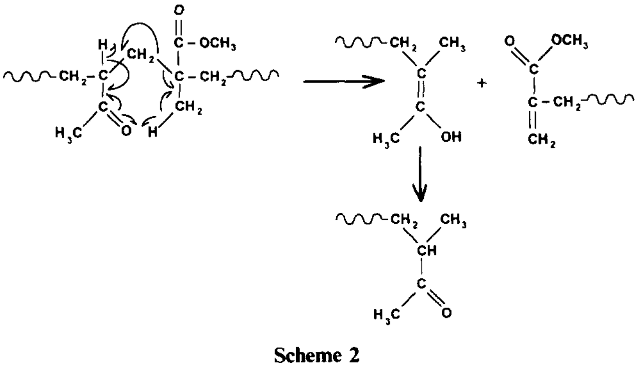
(Keywords: methyl methacrylate; aryl vinyl ketones; photolysis)

INTRODUCTION

We have shown that photolysis of methyl methacrylate (MMA)–methyl vinyl ketone (MVK) copolymers proceeds predominantly by a Norrish Type I mechanism (*Scheme 1*) to give allylic-ended oligomers[1,2] and not by a modified Norrish Type II process (*Scheme 2*), as proposed by Amerik and Guillet previously[3], although the Type II process does appear to be a minor contributor to the overall degradation process. This result was disappointing to us since the Type II process would have yielded polymerizable acrylic-ended oligomers, i.e. MMA macromonomers, and might have offered a novel and convenient route to prepare such materials. However, with low molecular weight ketones, the balance between Norrish Type I and Type II processes depends critically upon the structure of the ketone. Aryl alkyl ketones photolyse exclusively by a classic Norrish Type II mechanism[4,5] and this type of reaction is also greatly favoured in aromatic vinyl ketone homopolymers (polymers of the acrylophenone homologous series) that contain γ-hydrogens available for transfer, as required by the Type II mechanism[6,7]. Thus it was thought that the modified (non-classical) Norrish Type II mechanism (δ-hydrogen atom transfer), proposed by Amerik and Guillet for MMA–MVK photolysis (but found by us to be of only very minor importance compared with Norrish Type I photodegradation), might be similarly favoured in copolymers of MMA with vinyl aromatic ketones such as acrylophenone (AP), and also with its *p*-substituted derivatives, *p*-chloroacrylophenone (PCAP) and *p*-butylacrylophenone (PBAP), especially since it has been reported that homopolymers of *p*-substituted acrylophenones show increased quantum yields for Type II scission compared with polyAP itself[8–11], with the effect being greatest for polyPBAP. We thus report here studies of the oligomeric products produced by photolysing MMA–AP, MMA–PBAP and MMA–PCAP copolymers. We have concentrated upon determining the structures of the end groups on the oligomers, hoping to identify a situation in which the



Scheme 1



Scheme 2

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* For parts 1 and 2 in this series, see references 1 and 2
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modified Norrish Type II process is more favoured and hence one in which acrylic-ended oligomers are produced in significant quantities.

EXPERIMENTAL

Materials

MMA was freed from inhibitor (65 ppm hydroquinone monomethyl ether) by fractional distillation under reduced pressure, dried over Linde type 4A molecular sieves and stored in a freezer at −30°C until required.

AP was synthesized by dehydrochlorinating chloropropiophenone (Aldrich, 98%) following the method of Freedman *et al.*[12]. The product (a pale yellow oil) was obtained by fractional distillation (b.p. 70–72°C, 40 mmHg), in 78% yield, and displayed the expected ^{1}H n.m.r. and i.r. spectra. It was stored in a freezer at −30°C prior to use to prevent dimerization[13].

PBAP and PCAP were synthesized by Friedel–Crafts acylations of tert-butyl benzene (Aldrich, 99%) and chlorobenzene (Aldrich, 99%), respectively, with 3-chloropropionyl chloride (Aldrich, 98%) followed by dehydrochlorination of the intermediate chloropropiophenones. The procedures adopted were essentially those of Pizzirani *et al.*[14], Casey and Marvel[15] and Lukac *et al.*[8]. PBAP was obtained as an orange solid (yield 64%) and PCAP as a brown oil (yield 53%). (It should be noted that PBAP and PCAP are extreme skin irritants and will cause blistering on even slight skin contact. Unfortunately, the effect is not immediately evident, but develops over a period of a few hours following the initial contact.)

Synthesis of copolymers

All copolymers were prepared by free radical polymerizations of the appropriate monomer mixtures in sealed ampoules under vacuum in benzene at 60°C, using azoisobutyronitrile (AIBN) as initiator. The copolymers were recovered by precipitation in methanol and were purified by redissolution in chloroform and reprecipitation in methanol. The polymers were dried in a vacuum oven at room temperature before characterization and further use. Details of the copolymer preparations are given in *Table 1.*

Characterization of copolymers and oligomers

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

Table 1 Details of copolymer preparations

Copolymer no.	MMA (g)	Ketone (g)	AIBN (g)	C_6H_6 (ml)	Time (h)	Conversion (%)
MMA–AP						
1	10.02	1.50	0.015	23	22	78
2	10.05	5.95	0.014	19	18	63
MMA–PCAP						
3	15.07	3.31	0.033	24	22	17
4	19.74	4.70	0.035	17	26	30
MMA–PBAP						
5	5.00	2.83	0.032	11	24	36

Table 2 Details of copolymer analyses

Copolymer no.	Feed composition (mole fraction of ketone)	Copolymer composition (mole fraction of ketone)	M_n	D^a
MMA–AP				
1	0.10	0.07	132 000	1.80
2	0.25	0.29	129 000	1.86
MMA–PBAP				
3	0.19	0.14	54 000	2.33
MMA–PCAP				
4	0.05	0.13	40 000	1.83
5	0.06	0.13	46 000	1.65

^{a} *D*, polydispersity

U.v. photolyses

Copolymer solutions in benzene (2% w/v), contained in sealed quartz ampoules under vacuum, were photolysed in a Rayonet Photochemical Reactor, following previously published procedures[2]. The oligomeric products of photolysis were recovered by removal of the solvent on a rotary evaporator and were purified by redissolution in chloroform and precipitation in methanol.

RESULTS AND DISCUSSION

Copolymer analyses

Details of the copolymer analyses are given in *Table 2.* The copolymers of MMA with AP and PBAP are all slightly richer in MMA than the feeds from which they have been prepared whereas those of MMA and PCAP are less rich in MMA than the feed, indicating that PCAP has a slightly higher reactivity towards the MMA radical than has either AP or PBAP. The number-average molecular weights of all the copolymers are reasonably high (⩾40 000), a feature desirable if the oligomers prepared from them by photolysis are to have high concentrations of end groups other than those originally present in the starting polymers.

Copolymer photolyses

Details of the photolysis experiments on copolymers of MMA with AP, PCAP and PBAP are given in *Table 3.*

MMA–AP. As can be seen from *Table 3,* MMA–AP copolymers are photodegraded equally well by light of wavelengths 300 and 350 nm, with the average number of scissions per chain, *S*, increasing with time as expected. The ^{1}H n.m.r. spectrum in the region of the signals from the unsaturated end groups for the oligomeric products of one of the photolyses (run 2) is shown in *Figure 1a*; the spectra are similar for the products of runs 1 and 3. Although the end-group signals are very weak (owing to the relatively high average molecular weight of the oligomers), peaks attributable to olefinic methylene and olefinic methine protons of allylic end groups (protons labelled a, b and c in I) are visible, centred around 5.0 and 5.6 ppm, respectively. These signals are similar to those seen in the oligomers derived from photolyses of MMA–MVK copolymers[1,2]. Also visible, at 5.5 and 6.2 ppm, are much smaller peaks attributable to the

Table 3 Details of copolymer photolyses

Copolymer no.	Run no.	Polymer weight (g)	Wavelength (nm)	Time (h)	M_n	D	S
MMA-AP							
1	1	0.505	300	8	11 000	2.1	11
	2	0.545	300	27	7700	2.3	16
2	3	0.547	350	96	3500	2.2	36
MMA-PBAP							
3	4	0.557	350	77	4900	2.2	10
	5[a]	0.510	350	114	4200	2.3	12
MMA-PCAP							
4	6	0.567	350	67	23 000	28	–
5	7	0.545	350	64	23 000	19	–

[a] 20% v/v tert-butyl alcohol added to benzene solvent

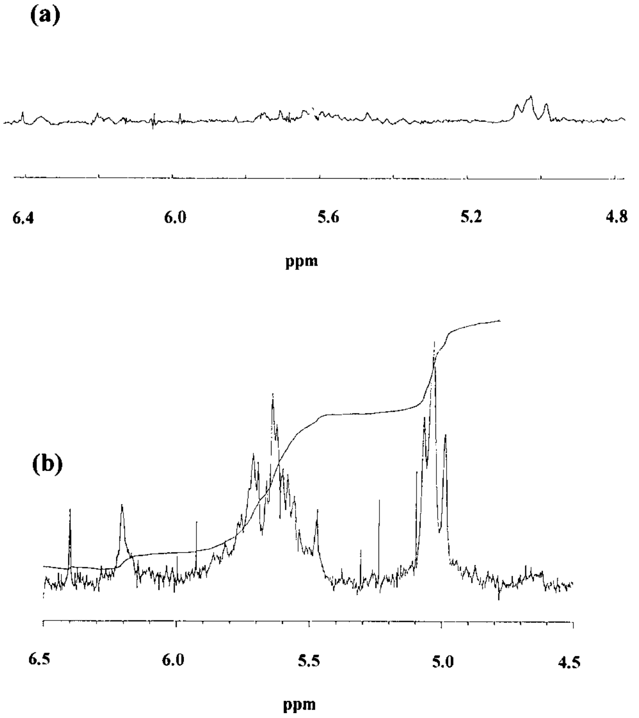
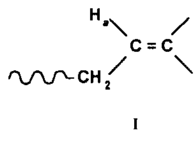


Figure 1 ^{1}H n.m.r. signals from unsaturated end groups in (a) an oligomer from MMA-AP photolysis (run 2) and (b) an oligomer from MMA-PBAP photolysis (run 5)

desired acrylic end groups (protons labelled d and e in II). Comparison of the areas of these various signals suggests that acrylic end groups form only 10% of the unsaturated ends, a proportion only marginally higher than that in the products from MMA-MVK photolysis (<8%)[2].



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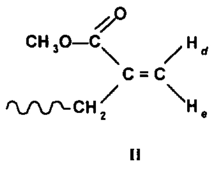

II

It appears, therefore, that the introduction of AP units, as opposed to MVK units, into a PMMA chain, increases to only a very minor extent the favourability of the modified Norrish Type II reaction. The effect is certainly less pronounced than that observed by Heskins *et al.* who found that the rate of the classic Type II reaction in styrene–AP copolymers was initially significantly greater than in styrene–MVK copolymers[13].

MMA-PBAP. The oligomers from runs 4 and 5 give identical ^{1}H n.m.r. spectra. That for the oligomers from run 5 in the region of the signals from unsaturated end groups is shown in *Figure 1b*. Clearly visible are the peaks from the olefinic methylene and olefinic methine protons at 5.0–5.1 and 5.5–5.8 ppm, respectively. Also visible are sharp peaks at 5.5 and 6.2 ppm from acrylic end groups. In addition, overlaid on the allylic methine signals, is a doublet of doublets at 5.65 and 5.75 ppm; this is assigned to the olefinic methylene signals of α,β-unsaturated ketone end groups arising from the photolysis of PBAP dyads and longer sequences, of which there are a significant number given that the copolymer contains 0.14 mol fraction of PBAP. Peaks at 5.65 and 5.75 ppm can also just be discerned in the spectra of the oligomers from MMA-AP copolymers (*Figure 1a*) and have a similar origin.

Integration of the various signals suggests that the three types of end group are approximately in the ratio: 1 acrylic : 3 allylic: 3 α,β-unsaturated ketone. This is an important result since it represents a much higher ratio of acrylic to allylic end groups than seen in the oligomers from either MMA-MVK or MMA-AP copolymers, and indicates that the relative amounts of Type I and modified Type II chain scission in MMA-alkyl vinyl ketone copolymers can indeed be influenced by the choice of the vinyl ketone unit. The particular effect of the *p*-tert-butyl group is probably to reduce the efficiency of the Norrish Type I process, thus allowing the modified Type II process to compete on more equal terms[16].

The introduction of tert-butanol in run 5 has had no discernible effect on the photolysis. This is in agreement with the work of Ng and Guillet[17] who concluded that the alcohol effect observed in small molecule ketone photolysis[18] (i.e. suppression of chain scission following a Norrish Type I process by stabilization of the intermediate biradical through hydrogen-bond interactions) is negligible for polymeric systems owing to compensating coil-contraction effects.

MMA-PCAP. The results of the photolyses of the MMA-PCAP copolymers are disappointing. In both cases, a significant gel fraction was formed and g.p.c. analyses of the sols showed bimodal distributions of molecular weight with unusually large polydispersities. It would appear that photolysis of MMA–PCAP copolymers consists of two competing reactions: chain scission and crosslinking. The most probable mechanism of crosslinking involves scission of the C–Cl bond followed by radical coupling. Little can be concluded from the poorly resolved ^{1}H n.m.r. spectra of the photolysis products.

CONCLUSIONS

Norrish Type I photodegradation of MMA–alkyl vinyl ketone and MMA–aryl vinyl ketone copolymers gives oligomers with allylic end groups whereas a modified Norrish Type II process gives oligomers with acrylic end groups. The balance between Norrish Type I and modified Norrish Type II photodegradation is dependent to a small extent on the nature of the alkyl or aryl vinyl ketone with the Type II process being most favoured (but still the minor component) in MMA–PBAP copolymers. It seems unlikely that a situation can be engineered in these systems where the Type I process will be the dominant component and therefore unlikely that the photodegradation of MMA–alkyl vinyl ketone and MMA–aryl vinyl ketone copolymers could be a viable route to polymerizable acrylic-ended macromonomers.

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