A GRAVIMETRIC AND SPECTROSCOPIC STUDY ON THE PHOTOINDUCED RADICAL CO-POLYMERISATION OF METHYL AND ALLYL METHACRYLATES: KINETIC AND STRUCTURAL PROPERTIES

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The photoinduced radical co-polymerisation of methyl and allyl methacrylates has been monitored by gravimetric analysis, Fourier Transform infra-red (FTIR) and FT nmr spectroscopy using a range of different photofragmenting and hydrogen atom abstracting type initiators. Using both visible and UV light sources the rates of photo-co-polymerisation were found to follow similar trends in both bulk and solution phase. Furthermore, unlike thermal polymerisation where crosslinking can occur through the allyl group, only the acrylate double bonds undergo reaction to produce a copolymer. GPC analysis showed that the homopolymers produced had narrower polydispersities than those of the copolymers while the photofragmenting type photoinitiators produced polymers with lower number average molecular mass than those produced via a hydrogen atom abstracting type. The latter is associated with marked differences in the degree of self-termination by initiator fragments. Structural analysis of the homo and copolymers by ^1H FT nmr showed that photoinduced polymerisations produce polymers with a greater degree of stereoregularity than those obtained by conventional thermal radical initiation. Thus, the initiating process appears to play a major role in controlling the orientation of propagating chains.

1. INTRODUCTION

The kinetics of photoinduced polymerisation of monomers and prepolymers has been widely investigated mostly as a means of assessing the activity and mechanism of photoinitiators as well as the physical characteristics of the crosslinked polymer[1,2]. Many methodologies have, in fact, been used to measure photopolymerisation kinetics[3]. In the laboratory one of the simplest systems applicable to non-crosslinkable vinyl monomers, such as methyl methacrylate, is the gravimetric method following precipitation in a non-solvent such as ethanol. This allows separation and characterisation of the polymer which can be beneficial in furthering our understanding of the mechanistic processes involved. Whilst the use of simple vinyl monomers has tended to be the norm for homopolymerisation, little work has been undertaken in terms of examining the photo-induced copolymerisation of simple acrylate monomers[1–3]. This is particularly so for monomers containing two

or more double bonds with differing reactivity. One notable case in point is allyl methacrylate which can lend itself to a two stage copolymerisation. Thus, in thermal radical induced polymerisation the methacrylic double bond can undergo ready reaction to form a normal, soluble, formable product while the second stage through the allyl group can form crosslinks, less efficiently, to give a thermoset structure[4].

Under photoinduced polymerisation only the acrylate group will polymerise. In this study therefore we have examined the photocopolymerisation of methyl and allyl methacrylate monomers in both bulk and solution media. A range of photofragmenting and hydrogen atom abstracting type photoinitiators have been used as illustrated in the structures shown using both visible and UV light irradiation. Using GPC the average molecular mass and polydispersities of the polymers have been obtained in order to provide information on initiator behaviour. The technique of FT nmr has also been used to monitor the rates of polymerisation and the data compared with that obtained by gravimetric and FTIR analysis. Through the former technique structural characteristics of the copolymer and homopolymers have also been determined for the first time and compared to those obtained by thermal induced polymerisation [5]. The implications of this work appear to be highly significant in terms of the stereoregularity of the photocopolymers which are not unlike those induced by anionic or cationic methodologies.

2. EXPERIMENTAL

2.1 Materials

The monomers, methyl (MMA) and allyl methacrylate (AMA) were obtained from the Aldrich Chemical Company Ltd., as were morpholine, anhydrous calcium chloride and azo-bis-isobutyronitrile and the HPLC grade solvents, chloroform, ethanol and 1,4-dioxane. Both the monomers were shaken with a 2% w/w sodium hydroxide solution followed by washing with double distilled water, drying overnight with calcium chloride and then vacuum distillation.

The three Irgacure photoinitiators, 369, 651 and 907 were obtained from Ciba-Geigy Ltd., Switzerland while the camphorquinone was obtained from the Aldrich Chemical Company Ltd., U.K. The 2-acrylamidoanthraquinone was synthesised as described earlier[6]. All the structures of the initiators used in this work are shown below.

2.2 Spectroscopic Measurements

FTIR spectra were obtained using a BIORAD FTS-7 instrument operated via an SPC-3200 data station while the FT nmr spectra were obtained using a JEOL 270.05 MHz GSX instrument in deuterated chloroform (Aldrich Chemical Company Ltd., U.K) using tetramethylsilane as the internal standard. Typical conditions for proton spectra were 32K data points; a pulse time of 3.3 microseconds at 25 °C and an acquisition time of 2.73 s. Spectra where appropriate (co-polymers) were deconvoluted using a Biosym Felix programme (version 2.3) from Biosym

Technologies Inc., Santiago, USA run on a Silicon Graphics INDY system.

2.3 Rates of Photopolymerisation

2.3.1 Gravimetric method

Solutions of the photoinitiators ($2 \times 10^{-3}M$) in the methyl and allyl methacrylate monomers in chloroform both in bulk and solution (50:50 v/v) were irradiated on an optical bench set-up utilising a 100 W high pressure Hg/W lamp (Phillips Laboratory Equipment, U.K) at 7 cm distance using the full wavelength spectrum in a pyrex tube fitted with a nitrogen inlet ($60^\circ C$). Morpholine was used as the co-initiator at $1 \times 10^{-3}M$ and the total volume of bulk monomers or solution irradiated was $10cm^3$. Copolymerisation experiments were undertaken in the same way using a 50:50 w/w of MMA and AMA. Aliquots of the irradiated monomer were added to ethanol and the precipitated polymer was filtered-off using a No.4 glass sintered filter, washed and then dried. Rates of polymerisation were obtained from plots of percentage conversion versus irradiation time[6]. The experimental weights of polymer obtained were repeatable within a 1% error.

Thermal polymerisations of the monomers were undertaken in bulk media at $80^\circ C$ using 0.1% of azo-bis-isobutyronitrile as initiator. Samples were taken at different times before gelation, cooled in an ice-water bath and then precipitated in ethanol, filtered via a No.3 glass sinter and then redissolved in toluene and refiltered. Solution polymerisations were undertaken in the same way in 1,4-dioxane as solvent.

2.3.2 FTIR method

Samples of the above monomers and solutions were also removed periodically and analysed by FTIR using a microcavity KBr cell with 0.1 mm path length and volume of 27 ml. The absorption band due to the vinyl deformation at 810 cm^{-1} was used to follow the reaction.

$$\text{Conversion} = 100 \times [(A_{810})_{t=0} - (A_{810})_{t=x}] / (A_{810})_{t=0}$$

2.3.3 FT nmr method

Samples of the monomers were also irradiated directly in NMR tubes (506-P, polished OD, length 178 mm, camber 0.025mm max and ID 4.2 mm) bubbling with a nitrogen stream via a finedrawn glass tube. The nmr signals at $\delta = 3.65$ ppm correspond to the methyl ester group and the integral is for 3 protons; the methylene ester group at $\delta = 4.62$ ppm and the integral is for 2 protons; and the two olefinic hydrogens at $\delta = 5.55$ ppm where the integral is for 1 proton each were used to follow the reactions.

$$\% \text{Conversion (MMA)} = 100 \times [(I_{5.55})_{t=0} \times 3 / (I_{3.65})_{t=0}] - [(I_{5.55})_{t=x} \times 3 / (I_{3.65})_{t=x}]$$

$$\% \text{Conversion (AMA)} =$$

$$100 \times [(I_{4.62})_{t=0} \times 3 / ((I_{3.65})_{t=0} \times 2)] - [(I_{4.62})_{t=x} \times 3 / ((I_{3.65})_{t=x} \times 2)]$$

$$\text{Proportion (Total)} = [(I_{5.55})_{t=0} \times 3 / (I_{3.65})_{t=0}] + [(I_{4.62})_{t=0} \times 3 / ((I_{3.65})_{t=0} \times 2)]$$

$$\text{Proportion (MMA)} = (I_{5.55})_{t=0} \times \text{Prop(total)} \times 3 / (I_{3.65})_{t=0}$$

$$\text{Proportion (AMA)} = (I_{4.62})_{t=0} \times \text{Prop(total)} \times 3 / (I_{3.65})_{t=0}$$

$$\% \text{Conversion (total)} = [(\% \text{Conversion})(\text{Prop})]_{\text{MMA}} + [(\% \text{Conversion})(\text{Prop})]_{\text{AMA}}$$

2.3.4 Gel Permeation Chromatography (GPC)

Weight and number average molecular weights of the polymer samples were analysed by the U.K Science and Engineering Research Council RAPRA service in Shrewsbury. The GPC/viscosity and conventional GPC (using PMMA equivalents) methods were used. Sample solutions were prepared by dissolving 20 mg of sample in 10 cm³ of tetrahydrofuran together with a trace of 1,2-dichlorobenzene as an internal marker. After dissolving overnight the solutions were then filtered through a 0.2 micron polyamide membrane. Each sample was run in duplicate on a PLgel 2 x mixed bed-B, 30 cm, 10 microns column at ambient temperatures at a flow rate of 1.0 cm³ per minute using viscosity/refractive index detectors.

3. RESULTS AND DISCUSSION

3.1 Rates of Photopolymerisation

The rates of photoinduced polymerisation using the Type I photofragmenting initiators, Irgacure, 651, 369 and 907 were obtained using UV irradiation while the Type II camphorquinone and 2-acrylamidoanthraquinone were examined under

visible light. The latter were found to exhibit lower photoactivity when using pyrex tubes under UV irradiation. The rates of photocopolymerisation of methyl and allyl methacrylates as measured by the gravimetric method are shown in Table 1. Under

TABLE 1

RATES OF PHOTOCOPOLYMERISATION MMA-AMA BY THE GRAVIMETRIC METHOD

PHOTOINITIATOR	$R_p \times 10^{-3} \text{ (mol s}^{-1} \text{ l}^{-1}\text{)}$ Bulk	$R_p \times 10^{-3} \text{ (mol s}^{-1} \text{ l}^{-1}\text{)}$ Solution
UV Hg LAMP 100 W		
IRGACURE 651	4.6	3.1
IRGACURE 369	6.7	3.7
IRGACURE 907	3.7	2.7
VISIBLE W/HALOGEN 100 W LAMP		
2-ACRYLAMIDOAQ+AMINE	2.8	1.9
2-ACRYLAMIDOAQ	0.6	0.4
CAMPORQUINONE	1.1	0.9
CAMPORQUINONE+AMINE	1.3	0.9

TABLE 2

RATES OF PHOTOCOPOLYMERISATION MMA-AMA BY THE FTIR METHOD

PHOTOINITIATOR	$R_p \times 10^{-3} \text{ (mol s}^{-1} \text{ l}^{-1}\text{)}$ Bulk	$R_p \times 10^{-3} \text{ (mol s}^{-1} \text{ l}^{-1}\text{)}$ Solution
UV Hg LAMP 100 W		
IRGACURE 651	2.3	1.8
IRGACURE 369	2.4	2.8
IRGACURE 907	2.2	1.3
VISIBLE W/HALOGEN 100 W LAMP		
2-ACRYLAMIDOAQ+AMINE	4.5	2.1
CAMPORQUINONE	1.8	0.8

TABLE 3

RATES OF PHOTOCOPOLYMERISATION MMA-AMA BY THE FT nmr METHOD

PHOTOINITIATOR	$R_p \times 10^{-3} \text{ (mol s}^{-1} \text{ l}^{-1}\text{)}$ Bulk	$R_p \times 10^{-3} \text{ (mol s}^{-1} \text{ l}^{-1}\text{)}$ Solution
UV Hg LAMP 100 W		
IRGACURE 651	3.4	2.5
IRGACURE 369	2.8	1.8
IRGACURE 907	4.8	3.3
VISIBLE W/HALOGEN 100 W LAMP		
2-ACRYLAMIDOAQ+AMINE	3.8	2.1
CAMPORQUINONE	1.6	1.0

UV irradiation in bulk and solution media the most effective Irgacure is 369 followed by 651 and then 907. In solution the rates are less owing to a combination of greater radical mobility giving rise to a higher rate of self termination as well as the possibility of chain-transfer by the solvent (chloroform). This would be expected to give rise to a lower molecular weight as will be discussed later. Under visible light irradiation the 2-acrylamidoanthraquinone was the most effective when used together with an amine co-synergist, morpholine. This was then followed by camphorquinone in conjunction with morpholine and then camphorquinone alone. The 2-acrylamidoanthraquinone was the least effective system when used alone. A similar trend was observed in solution media but again with lower rates of polymerisation.

The rates of photocopolymerisation by the FTIR method are compared in Table 2. Similar trends in polymerisation rates were found as those using the gravimetric method. Under visible light only two initiator systems were examined. Apart from Irgacure 369 the solution rates were much lower. Using the FT nmr method solution rates were also found to be lower but in the case of the Irgacure initiators the 907 system was the most effective followed by 369 and then 651. Under visible light irradiation the trends remain the same as for FTIR and gravimetric analysis. For comparison purposes the rates of photopolymerisation of MMA and AMA were measured in bulk only using Irgacure 651 and camphorquinone as photoinitiators. The data are shown in Table 4.

TABLE 4

RATES OF PHOTOPOLYMERISATION OF BULK MMA/AMA BY THE GRAVIMETRIC METHOD

PHOTOINITIATOR	$R_p \times 10^{-3} \text{ (mol s}^{-1} \text{ l}^{-1})$ MMA	$R_p \times 10^{-3} \text{ (mol s}^{-1} \text{ l}^{-1})$ AMA
UV Hg LAMP 100 W		
IRGACURE 651	3.9	6.1
VISIBLE W/HALOGEN LAMP 100W		
CAMPHORQUINONE	0.4	1.4

3.2 Spectroscopic Analysis of Polymers

3.2.1 FTIR

The homo and copolymers prepared by the gravimetric analysis method were analysed by FTIR and ^1H FT nmr techniques. A typical FTIR spectrum for the poly(co-methyl methacrylate allyl methacrylate) prepared using Irgacure 651 as photoinitiator in bulk after 60 minutes irradiation is shown in Figure 1. This is compared with the FTIR spectrum of a 50:50 w/w mixture of the corresponding monomers. The band at 1723 cm^{-1} for the comonomer mixture is shifted to

1731 cm^{-1} in the copolymer and corresponds to the C=O stretch of the same ester group while the band at 1169 cm^{-1} is the C–O stretch of the same ester in the comonomer mixture. The bands at 1178 and 1143 cm^{-1} in the copolymer correspond to the two asymmetric coupled C–O stretching vibrations, C–C(=O)–O– and O–C–C respectively. The olefinic C–H stretch has shifted from 1405 cm^{-1} in the comonomer to 1410 cm^{-1} in the copolymer. The band at 938 cm^{-1} due to the =CH₂ wagging modes in the comonomer has shifted to 930 cm^{-1} in the copolymer while the C–H deformation mode of the vinyl group has remained at 814 cm^{-1} . The comonomer exhibits two bands corresponding to the stretching vibrations of the allylic C=C bond and the methacrylic C=C at 1650 and 1638 cm^{-1} respectively, while the copolymer shows only one band at 1650 cm^{-1} due to the presence of unreacted allylic C=C groups. All the methacrylic C=C groups have reacted which is also evidenced by the shift in the methyl C–H doublet of the comonomer at 1300 and 1330 cm^{-1} to 1220 and 1260 cm^{-1} . Copolymers prepared in solution exhibited similar spectral changes.

Figure 1. FTIR spectra of a control mixture of 50:50 w/w methyl methacrylate/allyl methacrylate monomers (————) and poly(co-methyl methacrylate-allyl methacrylate) (-----) prepared using Irgacure 651 as photoinitiator in bulk after 60 minutes UV irradiation.

TABLE 5

MAIN ¹H FT nmr PEAKS FOR THE COPOLYMER OF MMA-AMA

STRUCTURAL ELEMENT	CHEMICAL SHIFT δ
CH ₃ -C- SYNDIOTACTIC	0.9
CH ₃ -C- ATACTIC	1.06
CH ₃ -C- ISOTACTIC	1.25
-C-CH ₂ -C-	1.4-2.4
CH ₃ -O-C(=O)-	3.6
=CH-CH ₂ -O-C(=O)-	4.6
CH ₂ =CH-CH ₂ -	5.23
CH ₂ =CH-CH ₂ -	5.9

3.2.3 FT nmr

The ^1H FT nmr spectra of the experimental samples produced in the copolymerisation of methyl and allyl methacrylates exhibit principal peaks which are summarised by the data in Table 5. These data also represent the main peaks observed for the homopolymers. There are three peaks at $\delta = 0.9$, 1.06 and 1.25 ppm which correspond to the Ca methyl groups in the syndiotactic, heteroatactic and isotactic fractions of the polymers. The corresponding methylene groups in all three fractions of the polymers occurs in the region $\delta = 1.4\text{--}2.4$ ppm. The methyl ester proton resonates at $\delta = 3.6$ ppm while the methylene ester protons in the allylic moiety resonate at $\delta = 4.6$ ppm. The peaks at $\delta = 5.23$ and 5.9 ppm due to the allylic group remain in the copolymer. A typical ^1H FT nmr spectrum of poly(allyl methacrylate) prepared after UV photoinduced polymerisation for 20 minutes using Irgacure 907 as photoinitiator is shown in Figure 2. Retention of the allylic groups are clearly seen. A typical spectrum of the poly(methyl methacrylate) obtained using visible light with camphorquinone as initiator for 60 minutes irradiation is illustrated in Figure 3. Here the high fractional ratio of syndiotactic to heteroatactic peaks is clearly seen. In all cases of photoinduced polymerisation it is noted that the ratio of syndiotactic to heteroatactic content is high. This is notable from a comparison of the spectrum shown in Figure 3 where the peaks at 0.9 and 1.06 ppm are markedly different for the photoinduced polymer of allyl methacrylate. For the thermally induced polymer as shown for PMMA the ratio is much closer. Ratios of syndiotactic and isotactic to the heteroatactic peak were then measured for all the homo and copolymers produced. The data for the homopolymers of MMA after 60 minutes of irradiation are shown in Table 6 compared with those obtained for a thermally induced polymer. The

TABLE 6

RATIO OF ISOTACTIC/SYNDIOTACTIC ^1H FTnmr PEAKS FOR THE BULK
HOMOPOLYMER OF MMA

INITIATION METHOD	SYNDIOTACTIC/HETERO ATACTIC	ISOTACTIC/HETERO ATACTIC
THERMAL	1.2:1	0.30:1
IRGACURE 651	2:1	0.40:1
CAMPBORQUINONE	2.5:1	0.40:1

syndiotactic portion is seen to be significantly greater with the camphorquinone giving rise to the highest ratio of 2.5:1. The isotactic fractions are only marginally higher in PMMA. Ratios for the homopolymers of AMA are compared in Table 7 after 60 minutes of irradiation. Again significantly higher ratios of syndiotactic to heteroatactic fractions are observed whereas the isotactic content is very low. In this case both camphorquinone and Irgacure 369 have produced the highest ratio of 3:1 and the data was independent of the time of irradiation. The copolymers of MMA-AMA also

Figure 2. Typical ^1H FT nmr spectrum of poly(allyl methacrylate) prepared in bulk after UV irradiation using Irgacure 907 as photoinitiator for 20 minutes.

Figure 3. Typical ^1H FT nmr spectrum of poly(methyl methacrylate) prepared in bulk after visible irradiation using camphorquinone as photoinitiator for 1 hour.

TABLE 7

RATIO OF ISOTACTIC/SYNDIOTACTIC ^1H FTNMR PEAKS FOR THE BULK
HOMOPOLYMER OF AMA

INITIATION METHOD	SYNDIOTACTIC/HETERO ATACTIC	ISOTACTIC/HETERO ATACTIC
THERMAL	1.2:1	0.85:1
IRGACURE 651	2:1	0.33:1
IRGACURE 907	2:1	0.26:1
IRGACURE 369	3:1	0.36:1
CAMPBORQUINONE	3.0:1	0.56:1

contain high ratios of syndiotactic fractions of upto 2:1. In this case data for a thermally induced copolymer could not be obtained due to the crosslinked nature of the material. This high degree of stereoregularity in the syndiotactic configuration is unusual and not previously reported on for photoinduced polymerisations. Whilst it is well known that the stereoregularity of acrylic polymers such as PMMA produced by thermal-induced radical polymerisation is dependent upon temperature⁷⁻⁹ the effects observed are significantly smaller than those observed in this study i.e. fractional increase of 0.1 over the temperature range 60 to -40°C . The structure of the photoinitiator also appears to play an important role here indicating that the configuration of the adding monomer to the propagating radical chain end is being controlled in some way by the photoinitiator. This suggests that this may involve some type of complex between the initiator and the monomer. Analysis of the absorption spectra of the photoinitiators in the presence of the monomers did not show any significant spectral shifts in this regard. However, low concentrations of addition of monomer to solutions of the photoinitiators ($<5\%$ v/v) were found not to change i.e. reduce the absorption band. In fact, the absorptions increased very slightly despite the apparent small dilution effect. This may indicate the possibility that a weak type of complexation is operative. Obviously, further research studies would be necessary before any concrete mechanism can be put forward.

3.3 Molecular Mass

Information on the molecular masses of the homo and copolymers are shown in Tables 9 and 10 respectively. Samples were again selected for analysis after 60 minutes of irradiation time for each photoinitiator type. For the homopolymer data it is noted that the hydrogen atom abstracting type camphorquinone produces a material with a significantly higher molecular weight than those of the photofragmenting types. This was also evidenced for the copolymers in both bulk and solution media (Table 10). In the case of the type I photofragmenting initiators a significantly higher number of chain terminating free radicals are formed¹ In solution media the molecular masses of the copolymers produced are also lower than those obtained in bulk. Here enhanced free radical mobility may be expected to increase the rate of self termination. However, the solvent used in the solution methods was chloroform which may also

TABLE 8

RATIO OF ISOTACTIC/SYNDIOTACTIC ^1H FTNMR PEAKS FOR THE BULK HOMOPOLYMER OF MMA-AMA

INITIATION METHOD	SYNDIOTACTIC/HETERO ATACTIC	ISOTACTIC/HETERO ATACTIC
THERMAL	CROSSLINKED	CROSSLINKED
IRGACURE 651	2:1	0.20:1
IRGACURE 907	1.5:1	0.21:1
IRGACURE 369	2:1	0.20:1
CAMPBORQUINONE	1.75:1	0.22:1
CAMPBORQUINONE/AMINE	2:1	0.24:1
2-ACRYLAMIDO AQ	2:1	0.33:1
2-ACRYALMIDO AQ/AMINE	2:1	0.20:1

TABLE 9

**GPC (PMMA EQUIVALENTS) AVERAGE MOLECULAR MASS AND
POLYDISPERSITIES OF THE BULK HOMOPOLYMERS OF MMA AND AMA**

PHOTOINITIATOR	M_w	M_n	M_w/M_n
PMMA			
IRGACURE 651	246,000	68,100	3.6
CAMPBORQUINONE	483,000	155,000	3.1
PAMA			
IRGACURE 651	195,000	57,100	3.4
IRGACURE 369	155,000	48,700	3.2
IRGACURE 907	233,000	75,600	3.1
CAMPBORQUINONE	589,000	153,00	3.9

TABLE 10

GPC (PMMA EQUIVALENTS) AVERAGE MOLECULAR MASS AND POLYDISPERSITIES OF THE BULK AND SOLUTION COPOLYMERS OF MMA-AMA

PHOTOINITIATOR	M_w	M_n	M_w/M_n
BULK			
IRGACURE 651	604,000	88,000	6.9
IRGACURE 369	509,000	90,900	5.6
IRGACURE 907	794,000	119,000	6.7
2-ACRYLAMIDOAQ/AMINE	346,000	65,600	4
CAMPHORQUINONE	1,370,000	318,000	4.3
SOLUTION			
IRGACURE 651	267,000	66,600	4
IRGACURE 369	137,000	60,800	2.3
IRGACURE 907	261,000	77,700	3.4
2-ACRYLAMIDOAQ/AMINE	287,000	75,100	3.8
CAMPHORQUINONE	638,000	143,000	4.5

suggest the possible implication of chain transfer processes through the well-known formation of the dichloromethylene radical. The polydispersities of the copolymers are also higher than those obtained for the homopolymers although they are fairly typical for a free radical polymerisation of this type.

4. CONCLUSIONS

The photoinduced radical co-polymerisation of methyl and allyl methacrylates has been monitored using different techniques under both visible and UV light irradiation. The rates of photo-co-polymerisation were found to follow similar trends in both bulk and solution phase and only the acrylate double bonds reacted to produce a copolymer. GPC analysis showed that the homopolymers produced have narrower polydispersities than those of the copolymers while the photofragmenting type photoinitiators produced polymers with lower number average molecular mass than those produced via a hydrogen atom abstracting type. Structural analysis of the homo and copolymers by ^1H FT nmr showed that photoinduced polymerisations produce polymers with a greater degree of stereoregularity in the syndiotactic configuration than those obtained by conventional thermal radical initiation. Thus, the initiating species appear to play a major role in controlling the orientation and addition of the monomer to the propagating radical chains. Corroborative evidence in support of this work originates from a recent study on the photoinduced polymerisation of methyl methacrylate monomer in the presence of zinc oxide where highly syndiotactic polymer was produced[10]. Our irradiation conditions were carried out at 60 °C, therefore Tg is not crucial here. Also, the variation in tacticity between the different photoinitiators requires further detailed work.

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