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Control of stereoregularity in poly(methyl methacrylate) by photoinitiated polymerization

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Abstract

Poly(methyl methacrylate) was prepared by photoinduced bulk polymerization using a variety of radical and cationic initiators together with amine cosynergists. Any effects which may have arisen due to differences in temperature were excluded by carrying out a peroxide-initiated thermal polymerization at the same temperature as the photopolymerizations. Molar masses were characterized by gel permeation chromatography. Values of the weight-averaged molar mass were all less than 10^5 g mol^{-1} and the polydispersities were typical of a very broad distribution of free-radical addition processes. Proton Fourier-transform nuclear magnetic resonance was used to monitor any stereoregularity. By determining the ratio of syndiotactic to heteroatactic peaks, it was found that the photoinitiated polymers were predominantly syndiotactic, with the thermally initiated polymers showing much less syndiotactic character. The configuration was strongly dependent on the type of photoinitiator and amine cosynergist. All the hydrogen-abstracting photoinitiators gave polymers with unimodal distributions, except 1-chloro-4-propoxythioxanthone. This, together with the photofragmenting initiator Irgacure 369 and the cationic complex Irgacure 261, gave bimodal distributions. Such distributions suggest that competitive processes are operating during the reaction. This may be one reason responsible for the unexpected behaviour of 1-chloro-4-propoxythioxanthone, which has recently been shown to dehalogenate on irradiation, possibly inducing cationic character. With regard to the amine cosynergists, dicyclohexylamine facilitated higher stereospecificity.

Keywords: Photoinitiated polymerization; Poly(methyl methacrylate); Stereoregularity

1. Introduction

Poly(methyl methacrylate) (PMMA) is a linear thermoplastic which is predominantly syndiotactic (70%–75%) when produced by free-radical addition polymerization and predominantly isotactic when produced by anionic polymerization. PMMA produced commercially is usually made by free-radical reactions, via bulk or suspension polymerization, resulting in average molar masses of approximately 10^6 and approximately 10^5 g mol^{-1} respectively. In general, polymers prepared using free-radical initiators are predominantly syndiotactic, and the tendency to form syndiotactic sequences increases as the temperature is lowered. The end-unit of the chain, being a free radical, is unable to maintain asymmetry, and is either planar or oscillates rapidly between two possible tetrahedral configurations. Hence there is no permanent spatial position for the terminal carbon radical. However, the penultimate unit does take up a single tetrahedral configuration and must be either syndiotactic or isotactic with respect to the previous asymmetric carbon. Therefore, for steric reasons, syndiotactic propagation should be slightly favoured energetically over isotactic propagation.

On this basis, it is expected that photoinduced polymerizations of acrylic esters will proceed via a homogeneous free-radical addition process, typical of that for commercial peroxide-initiated thermal polymerizations, to yield syndiotactic material. Earlier work [1] on emulsion photopolymerization of methyl methacrylate showed that the polymer was formed with a higher than normal degree of syndiotacticity when compared with that produced by a typical homogeneous free-radical polymerization. More recent work has shown that highly syndiotactic PMMA is produced when zinc oxide is used as the initiator [2]. In both of these studies, the heterogeneous nature of the phases is an important factor in controlling the orientation of the growing free-radical chains. In the former case, the excited state of the photoinitiator has altered geometry, dipole moment, electron-donating and electron-accepting ability and acid–base properties when compared with its parent ground state. In these ways, the new steric arrangements of the initiator may influence the orientation of any addition.

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In an earlier study [3], we confirmed the work by Turro et al. [1] on emulsion photopolymerization, and found that both homopolymers and copolymers of methyl and allyl methacrylates exhibited a degree of stereoregularity in the syndiotactic configuration, when produced by photoinitiated free-radical polymerization, which surpassed that for the corresponding thermal polymerization. Here the syndiotacticities were found to be independent of the rates and extent of reaction as well as the initiator concentration. The observation of a high degree of syndiotactic orientation in a homogeneous, free-radical-photoinduced matrix has led us to extend the investigation to cover a wider range of initiators. These encompass free-radical-photofragmenting, hydrogen-atom-abstracting and cationic types. They include a new halogenated thioxanthone which undergoes photodehalogenation giving rise to subsequent acid generation. Because amine cosynergists may be used together with photoinitiators, these have also been examined.

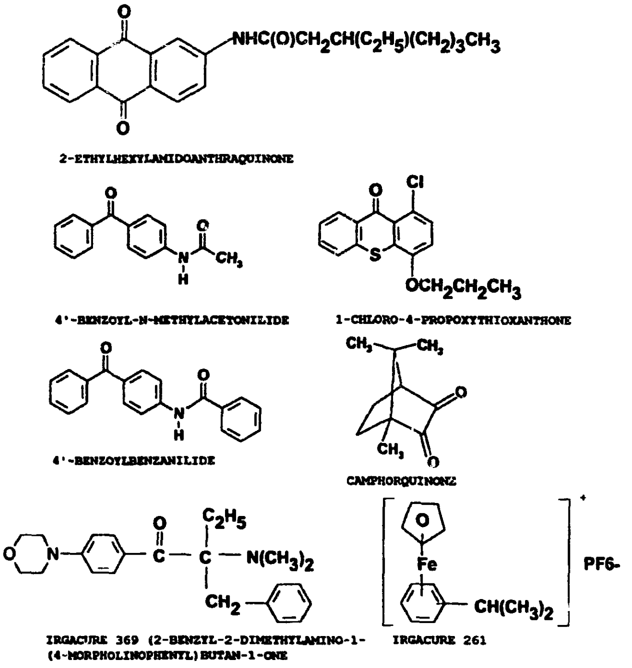
2. Experimental details

2.1. Materials

Methyl methacrylate, anhydrous calcium chloride, lauryl peroxide, sodium hydroxide, camphorquinone, spectroscopic grade ethanol, triethylamine, dicyclohexylamine, tert-butylamine, tri-*n*-butylamine, dimethylaniline and aniline were obtained from Aldrich Chemical Company, Gillingham, Dorset, UK. Methyl methacrylate was shaken with 2% sodium hydroxide solution to remove the inhibitor. This was followed by washing with doubly distilled water, drying overnight with anhydrous calcium chloride and vacuum distillation. The initiators, Irgacure 369 and 261, were obtained from Ciba-Geigy Ltd., Manchester, UK and were used as received. 1-Chloro-4-propoxythioxanthone, 4′-benzoyl-*N*-methylacetonilide and 4′-benzoylbenzanilide were obtained from Great Lakes Ltd., Widnes, UK. 2-Ethyl-*n*-hexylamidoanthraquinone was synthesized in our laboratory as described previously [4]. The structures of all the photoinitiators are shown in Scheme 1.

2.2. Photopolymerization

Solutions of the photoinitiators and amines (5×10^{-5} M) in methyl methacrylate (10 cm^3) were irradiated on an optical bench set-up with a 100 W high pressure Hg lamp (Philips Laboratory Equipment, UK) at a distance of 9 cm using the full wavelength spectrum in a Pyrex tube fitted with a nitrogen gas inlet (60 °C) which also ensured mixing. After 1 h of irradiation, the mixture was poured into ethanol and the precipitated polymer was filtered off using a No. 4 glass sintered filter, washed and then dried to constant weight at 60 °C. The experimental weights were repeatable within 1% error. Shorter and longer experimental periods have been investigated previously [3] and were found to give consistent data in terms of syndiotacticity.



Scheme 1. Structures of photoinitiators.

Methyl methacrylate was also thermally polymerized at 60 °C using 0.1% w/w of lauryl peroxide as initiator over a water bath for 72 h. Purification of the polymer was undertaken as described above and the experiment was repeated to give consistent results.

2.3. Gel permeation chromatography (GPC)

The weight- and number-averaged molecular weights of the polymer samples were obtained by the UK Science and Engineering Research Council RAPRA Service (Shrewsbury). The GPC/viscosity and conventional GPC (using PMMA equivalents) methods were used. Sample solutions were prepared by dissolving 20 mg of polymer in 10 cm^3 of tetrahydrofuran together with a trace of 1,2-dichlorobenzene as internal marker. After dissolving overnight, the solutions were filtered through a 0.2 μm polyamide membrane. Each sample was run in duplicate/triplicate on a PL-gel 2 × mixed bed-B (30 cm, 10 μm) column at ambient temperatures at a flow rate of 1.0 cm^3 min^{-1} using viscosity/refractive index detectors. The molecular weights were accurate within 1%–2% and the values given are the averages of duplicate sets of data.

2.4. ^{1}H Fourier-transform nuclear magnetic resonance (FTNMR) analysis

Samples of polymer were measured in deuterated chloroform (Aldrich Chemical Co. Ltd., UK) using a JEOL 270.05 GHz GSX instrument with tetramethylsilane as the internal

Table 1
Percentage conversion (1 h) and average molecular mass (GPC) (g mol^{-1}) for bulk homopolymer of MMA using different photoinitiators (5×10^{-3} M)

Photoinitiator	Conversion (%)	M_w (g mol^{-1})	M_n (g mol^{-1})	Polydispersity
Irgacure 369	24.11	113 500	20 150	5.7
Irgacure 261	2.92	449 000	98 000	4.6
Camphorquinone	0.56	483 000	155 000	3.1
2-Ethylhexylamidoanthraquinone	0.05	–	–	–
1-Chloro-4-propoxythioxanthone	0.29	340 000	52 500	6.5
4′-Benzoylbenzanilide	0.01	407 000	36 700	11
4′-Benzoyl-*N*-methylacetonilide	0.35	451 500	109 000	3.7

Table 2
Percentage conversion (1 h) and average molecular mass (GPC) (g mol^{-1}) for bulk homopolymer of MMA using different photoinitiators (5×10^{-3} M) and triethylamine (5×10^{-3} M)

Photoinitiator	Conversion (%)	M_w (g mol^{-1})	M_n (g mol^{-1})	Polydispersity
Irgacure 369	22.28	230 000	23 150	9.8
Irgacure 261	5.11	634 000	73 000	8.9
Camphorquinone	8.1	180 000	77 800	2.3
2-Ethylhexylamidoanthraquinone	0.4	39 500	22 850	1.8
1-Chloro-4-propoxythioxanthone	0.26	124 000	34 100	3.6
4′-Benzoylbenzanilide	0.17	–	–	–
4′-Benzoyl-*N*-methylacetonilide	1.02	250 500	42 000	5.9

Table 3
Percentage conversion (1 h) and average molecular mass (GPC) (g mol^{-1}) for bulk homopolymer of MMA using Irgacure 369 (5×10^{-3} M) and different amines (5×10^{-3} M)

Amine	Conversion (%)	M_w (g mol^{-1})	M_n (g mol^{-1})	Polydispersity
Triethylamine	22.28	230 000	23 150	9.8
Dicyclohexylamine	21.18	96 100	28 000	3.4
tert-Butylamine	19.45	115 500	21 400	5.4
Tri-*n*-butylamine	18.19	105 500	32 800	3.2
Dimethylamine	20.53	94 600	21 200	4.5
Aniline	23.54	111 500	28 900	3.9

standard. Typical conditions for proton spectra were 32 K data points, a pulse time of 3.3 μs at 25 °C and an acquisition time of 2.73 s. Spectra were deconvoluted using a Biosym Felix Program (version 2.3) from Biosym Technologies Inc., Santiago, USA run on a Silicon Graphics Indy System (off-line).

3. Results and discussion

3.1. Molar mass distributions and polydispersities

In order to avoid interference from post-degradation products, but to achieve reasonable yields, photoconversions were followed for 1 h of irradiation only. Variable periods of irradiation have been examined previously and have been found to be unimportant in terms of the syndiotactic content. The percentage conversions, average molecular weights and polydispersities are shown in Tables 1–4. The first set of data in Table 1 shows the effect of photoinitiator alone. The most significant feature arising from these data is the high conversion for Irgacure 369 compared with all the other photoinitiators. This is offset by a significantly lower average molar mass. The polydispersities vary significantly and are very high in a number of cases, indicating a possible high degree of self-termination giving rise to a series of low molecular weight products. The absence of any values in the tables indicates that the physical nature of the samples rendered them unsuitable for GPC measurements. Table 2 gives data for the same initiators in the presence of triethylamine. Use of the amine provides slightly higher conversions and notably higher average molecular weights, especially for Irgacure 369 and 261. Both of these initiators operate via a photofragmentation process, with Irgacure 261 operating via a cationic mechanism. Here, primary radicals from the photoinitiator are removed by the amine to form alkylamino radicals; the latter then promote polymerization. When a range of amines is evaluated (Table 3), the most effective is triethylamine. However, the structural dimensions of the other amines may be a contributing factor. With the type II hydrogen-atom-abstracting photoinitiators, the presence of the amine induces the rapid formation of ketyl-type radicals and leads to com-

Table 4
Percentage conversion (1 h) and average molecular mass (GPC) (g mol^{-1}) for bulk homopolymer of MMA using camphorquinone (5×10^{-3} M) and different amines (5×10^{-3} M)

Amine	Conversion (%)	M_w (g mol^{-1})	M_n (g mol^{-1})	Polydispersity
Triethylamine	8.1	180 000	77 800	2.3
Dicyclohexylamine	10.99	350 500	87 000	4.1
tert-Butylamine	7.78	22 800	102 000	2.3
Tri-*n*-butylamine	7.93	111 000	27 000	4.2
Dimethylamine	10.41	138 000	61 200	2.3
Aniline	1.54	279 000	53 500	5.2

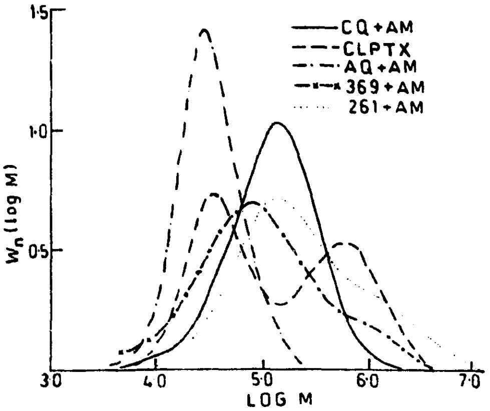


Fig. 1. Molecular mass distribution curves of PMMA samples prepared by photoinduced polymerization using camphorquinone and triethylamine (———), 1-chloro-4-*n*-propoxythioxanthone (– – –), 2-ethylhexylanthraquinone and triethylamine (– · –), Irgacure 369 and triethylamine (– × –) and Irgacure 261 and triethylamine (· · ·) (5×10^{-3} M each).

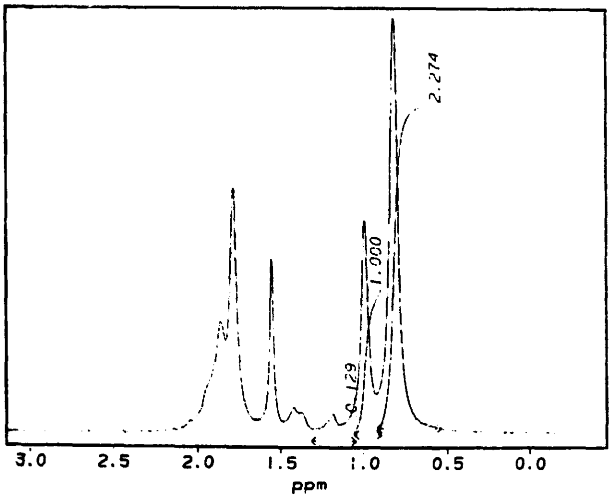


Fig. 2. Deconvoluted ^{1}H FTNMR spectrum of PMMA prepared using Irgacure 261 and triethylamine (5×10^{-3} M each) in the region 3.0–0.0 ppm.

petitive termination processes with the alkylamino radicals. This is supported by the significantly lower average molecular weights for the camphorquinone–amine systems (Table 4). In fact, the data in Table 4 indicate the formation of narrower polydispersities than those obtained using Irgacure 369. All the values were precise to within 1%–2%.

The molar mass distributions are plotted in Fig. 1 to reveal three salient features. The first is that all the polymers derived from the use of type II hydrogen-atom-abstracting photoinitiators (2-ethylhexylamidoanthraquinone and camphorquinone as examples) exhibit broad unimodal distributions. The second is that the photofragmenting photoinitiator (Irgacure 369) and the cationic system (Irgacure 261) give polymers which exhibit bimodal distributions. The third is that a marked bimodal distribution curve results for 1-chloro-4-*n*-propoxythioxanthone.

The bimodal distributions indicate the involvement of competitive reaction processes during photopolymerization. Although this is expected for the photofragmenting initiators (where competing radicals may be involved) and for the cationic systems (where radical cations as well as radicals can result in a complex sequence of reactions) [5], it is surprising for 1-chloro-4-*n*-propoxythioxanthone. However, this initiator has recently been shown to proceed through a mechanistic sequence which initially involves dehalogenation to produce a chlorine radical [6]. The competitive nature of this species during free-radical polymerization when coupled with hydrogen-atom abstraction could certainly give rise to other reactions. The subsequent formation of hydrogen chloride would follow to give rise to a sequence of "cationic" processes.

3.2. Stereoregularity

The ^{1}H FTNMR spectra of all the polymer samples were deconvoluted for comparative purposes. Gaps in the tables indicate difficulties in sample measurement or in the resolution of the peaks. The ^{1}H FTNMR spectra of PMMA are characterized by three types of proton: three equivalent ester methyl protons which appear as a singlet at $\delta = 3.6$ ppm and contain no stereochemical information, two β-methylene protons at $\delta \approx 2.0$ ppm and three equivalent α-methyl protons at $\delta \approx 1.2$ ppm. Syndiotactic PMMA has a twofold axis of symmetry, and the two geminal methylene protons are in equivalent environments and are thus seen as a singlet. For isotactic PMMA, the methylene protons are non-equivalent and, provided that there is no vicinal coupling, two doublets are observed with a spacing equal to geminal coupling. Although we might expect the α-methyl protons to exhibit a similar behaviour to the ester methyl protons, three bands appear corresponding to three different chemical shifts of the possible monomeric triads: syndiotactic, heteroatactic and isotactic at $\delta = 0.9$, 1.06 and 1.25 ppm respectively.

Table 5
Ratio of syndiotactic and isotactic to heteroatactic ^{1}H FTNMR peaks for bulk homopolymer of MMA using different photoinitiators (5×10^{-3} M)

Photoinitiator	Syndiotactic/heteroatactic	Isotactic/heteroatactic
Irgacure 369	2.42 : 1	0.14 : 1
Irgacure 261	2.09 : 1	–
Camphorquinone	2.50 : 1	0.40 : 1
2-Ethylhexylamidoanthraquinone	2.17 : 1	–
1-Chloro-4-propoxythioxanthone	2.60 : 1	–
4′-Benzoylbenzanilide	–	–
4′-Benzoyl-*N*-methylacetonilide	1.72 : 1	0.55 : 1

Table 6
Ratio of syndiotactic and isotactic to heteroatactic ^{1}H FTNMR peaks for bulk homopolymer of MMA using different photoinitiators (5×10^{-3} M) and triethylamine (5×10^{-3} M)

Photoinitiator	Syndiotactic/heteroatactic	Isotactic/heteroatactic
Irgacure 369	2.40 : 1	0.19 : 1
Irgacure 261	2.33 : 1	0.18 : 1
Camphorquinone	2.65 : 1	–
2-Ethylhexylamidoanthraquinone	2.50 : 1	0.06 : 1
1-Chloro-4-propoxythioxanthone	2.23 : 1	0.14 : 1
4′-Benzoylbenzanilide	–	–
4′-Benzoyl-*N*-methylacetonilide	2.23 : 1	0.08 : 1

Table 7
Ratio of syndiotactic and isotactic to heteroatactic ^{1}H FTNMR peaks for bulk homopolymer of MMA using Irgacure 369 (5×10^{-3} M) and different amines (5×10^{-3} M)

Amine	Syndiotactic/heteroatactic	Isotactic/heteroatactic
Triethylamine	2.42 : 1	0.14 : 1
Dicyclohexylamine	2.89 : 1	0.53 : 1
tert-Butylamine	1.84 : 1	0.40 : 1
Tri-*n*-butylamine	2.02 : 1	0.10 : 1
Dimethylamine	1.81 : 1	0.08 : 1
Aniline	1.87 : 1	0.08 : 1

Table 8
Ratio of syndiotactic and isotactic to heteroatactic ^{1}H FTNMR peaks for bulk homopolymer of MMA using camphorquinone (5×10^{-3} M) and different amines (5×10^{-3} M)

Amine	Syndiotactic/heteroatactic	Isotactic/heteroatactic
Triethylamine	2.65 : 1	–
Dicyclohexylamine	2.72 : 1	0.19 : 1
tert-Butylamine	2.05 : 1	0.06 : 1
Tri-*n*-butylamine	2.1 : 1	0.14 : 1
Dimethylaniline	2.08 : 1	0.11 : 1
Aniline	1.92 : 1	0.22 : 1

To ascertain the stereoregularity, the peak integrals were related to the heteroatactic peak at 1.06 ppm, which was set at a value of 1.0. A typical deconvoluted spectrum is shown in Fig. 2 for a polymer prepared using Irgacure 261 as the initiator. It should be noted that, on deconvolution, the peaks shift slightly to lower fields. The ratios of the peak heights of the syndiotactic and isotactic fractions are compared in Tables 5–8. All the photoinitiators give rise to polymers with high fractions of syndiotactic configuration (Table 5). When the amine cosynergist is added, it gives, in many cases, higher values compared with that observed for the initiator alone (Table 6). Dicyclohexylamine is notable in this regard with a peak ratio of approximately 3 : 1 in combination with Irgacure 369 (Table 7) and camphorquinone (Table 8). Only low levels of isotactic sequences are observed in all cases.

In contrast, thermally polymerized PMMA is less stereoregular, as typified by lower peak ratios. This has been attributed to the higher temperatures (40–90 °C) involved in

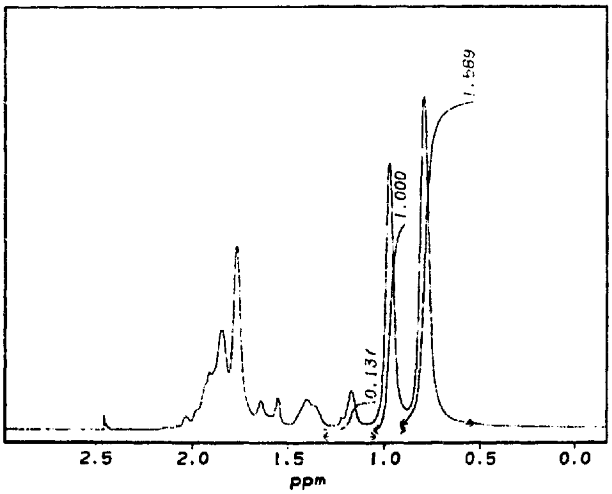


Fig. 3. Deconvoluted ^{1}H FTNMR spectrum of PMMA prepared using lauryl peroxide (0.1%, w/w) at 60 °C for 72 h in the region 3.0–0.0 ppm.

homogeneous radical polymerization [3]. In order to eliminate such an effect, we prepared a peroxide-induced polymer sample at the same temperature (60 °C) as that used in the photoinduction experiments. Using lauryl peroxide as the initiator, the reaction took 72 h to yield enough polymeric material for analysis. This sample had a weight-averaged molecular weight of 750 000 g mol^{-1}. The ^{1}H FTNMR spectrum of the polymer is shown in Fig. 3, where it is seen that the peak integrals are comparable with those of thermal induced polymerization [7]. Thus, it is evident that the amount of syndiotactic material is less than that observed for the photoinitiated reactions. For example, when Irgacure 261 is used as the photoinitiator, the ratio of syndiotactic to heteroatactic peaks is approximately 2.1 : 1, but when lauryl peroxide is used to initiate thermal polymerization, the ratio of these peaks is approximately 1.3 : 1.

Perhaps the most interesting observation in this study is the variability engendered by the type of photoinitiator and amine cosynergist used. The photoinitiator and monomer form a complex, as observed in laser photolysis studies [5]. How this dictates polymer tacticity is uncertain. One feasible explanation is that, within this complex, the triplet state exhibits stereospecificity controlling the orientation of the incoming monomer. The bulkiness of dicyclohexylamine may be important in this context.

4. Conclusions

This study has demonstrated that more stereoregular PMMA may be produced by photoinitiated polymerization than by thermally initiated polymerization. In general, the polymers which result are highly syndiotactic, but further control of the stereoregularity can be made possible by a careful choice of photoinitiator. The efficiency is improved by the use of amine cosynergists, with dicyclohexylamine culminating in unusually high stereospecificity. For all combinations, the performance was determined by comparing the ratio of syndiotactic to heteroatactic peaks in the FTNMR spectra, where values of approximately 3 : 1 were achieved.

In terms of molecular weight, the photofragmenting initiators (Irgacure 369 and the cationic complex Irgacure 261) give polymers with bimodal distributions, suggesting the involvement of competitive reaction processes during polymerization. All the hydrogen-atom-abstracting-type photoinitiators give polymers with unimodal distributions, this being typical of such polymerization processes. An exception is 1-chloro-4-propoxythioxanthone. This is associated with dehalogenation to give radicals, which may effect cationic characteristics. The strong bimodal distribution observed for 1-chloro-4-propoxythioxanthone indicates the involvement of competitive processes similar to those of cationic or photofragmenting-type systems.

The reason for the preferred tacticity is perhaps centred in the geometry of the excited state of the photoinitiator. The stereospecific nature of an associated complex between initiator and monomer may be used to control the orientation of the incoming monomer and so force the growing polymer chain to adopt a specific configuration. Work is currently underway to elucidate some of these features of photopolymerization.

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