

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Synthesis of Poly(glycidyl Methacrylate-*r*-photochromic Monomer) by ATRP

Mildred Flores-Guerrero^a; Luis. E. Elizalde^a; Gladys De Los Santos-Villarreal^a

^a Centro de Investigacion en Quimica Aplicada Blvd., Enrique Reyna Hermosillo # 140, Saltillo, Coahuila, México

To cite this Article Flores-Guerrero, Mildred , Elizalde, Luis. E. and Santos-Villarreal, Gladys De Los(2009) 'Synthesis of Poly(glycidyl Methacrylate-*r*-photochromic Monomer) by ATRP', Journal of Macromolecular Science, Part A, 46: 3, 223 – 231

To link to this Article: DOI: 10.1080/10601320802637045

URL: <http://dx.doi.org/10.1080/10601320802637045>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Synthesis of Poly(glycidyl Methacrylate-*r*-photochromic Monomer) by ATRP

MILDRED FLORES-GUERRERO, LUIS. E. ELIZALDE* and GLADYS DE LOS SANTOS-VILLARREAL

Centro de Investigacion en Quimica Aplicada Blvd., Enrique Reyna Herosillo # 140, Saltillo Coahuila 25100, México

Received August 2008, Accepted September 2008

The preparation of the random photochromic copolymer poly(glycidyl methacrylate-*r*-1'-(2-methacryloxyethyl)-6-nitro-3',3'-dimethylspiro-[2H-1]-benzopyran-2,2'-indoline) by ATRP is reported, which can be used for the preparation of smart materials. Narrow homopolymers obtained from glycidyl methacrylate (GMA) are prepared when HMTETA-copper bromide and ethyl 2-methyl-2-bromo-propionate are used as the catalytic system with methyl-ethyl-ketone at 50°C. By using a molar ratio of 1:1 ligand: initiator, good correlations between experimental and theoretical molecular weights and narrow molecular weight distribution are obtained. These experimental conditions are also employed for the copolymerization of GMA with a photochromic monomer, where again good control of the polymerization reaction is obtained. The copolymer is fully characterized by spectroscopic techniques. The reactivity ratios are calculated according to the extended Kelen-Tüdös method, while the composition of the copolymer is calculated by NMR. Determination of r_{GMA} and r_{PHM} gives a value of 0.985 for GMA and 0.596 for the photochromic monomer.

Keywords: Photochromic copolymer, ATRP, glycidyl methacrylate, spirobenzopyrane indoline

1 Introduction

The synthesis and polymerization of functional monomers have attracted much attention lately because of their vast versatility to incite further modification over their chemical structures. Additionally, the development of the living polymerization techniques has also unfurled a growing field in the preparation of polymeric functional materials in a well-controlled condition. Glycidyl methacrylate (GMA) is a functional monomer which contains a reactive oxirane ring on its structure, with this functionality the polymer obtained is able to react with several nucleophile entities and can be used in several industrial (1,2) and technological applications (3–7). For such applications, the smart materials are one of the most promising topics, since some of them can respond to an external impulse, such as changes in the refraction index, redox reactions, color change, etc. One of these types of compounds can be used for the preparation of smart materials which could react reversibly with the electromagnetic radiation and be known as a photochromic compound. Its molecule absorbs ultraviolet light and modifies its chemical structure through the generation of a highly

conjugated π system (8) which produces color in the visible region.

Derivatives of spirobenzopyrane indoline and spirobenzoxazine photochromic compounds have been widely employed in the development of several optical devices, the most common of which is the manufacturing of photoresponsive eyeglasses, optical lenses, waveguides, photochromic films and erasable storage media. These applications require the synthesis of very stable molecules in order to get an indefinite number of reversible cycles of coloration-discoloration before the eventual degradation of the photoactive molecules. Additionally, it is important to avoid scratching the surface during the manipulation of the prepared materials so as to prevent from damaging the optical properties. The way to overcome the scratching problem is to use hard materials as the matrix which would provide support for the photochromic molecules to yield adequate mechanical strength to stabilize materials for a long time. Several methods regarding the use of functional monomers such as GMA are reported in the literature. GMA is able to polymerize through the acrylic functionality, and can also be crosslinked by photopolymerization through the highly reactive oxirane ring (9–11).

The polymerization of GMA through the acrylic moiety has been known for several decades, however, little attention has been focused on its reaction by a living-controlled polymerization method. The main topics of controlled polymerizations are: (a) their versatility in using functional monomers, (b) the possibility of synthesizing

*Address correspondence to: Luis. E. Elizalde, Centro de Investigacion en Quimica Aplicada Blvd., Enrique Reyna Herosillo # 140, Saltillo Coahuila 25100, México; E-mail: elizalde@ciqa.mx

polymers with highly controlled architecture and molecular weight, and (c) the low polydispersity index (PDI) obtained. Additionally, good control on the stereoregularity of methacrylic polymers has been found when ytterbium salts were used as catalysts (12–15).

Focusing on controlled living radical polymerization techniques, Atom Transfer Radical Polymerization (ATRP) is one of the most widely employed polymerization methods. One of the first attempts on the homopolymerization of glycidyl monomers by ATRP was performed by Matyjaszewski (16) who reported the use of CuBr(I)/4,4'-di-(5-nonyl)-2-2'-bipyridine (dNbipy) as the catalytic system initiated by halogenated compounds at 90°C. Recently, Krishnan and Srinivasan (17) reported in a short communication the polymerization of GMA by ATRP where the oxirane ring has kept its chemical integrity. In this particular case, the catalytic system used was CuBr(I)/N-(n-propyl)-2-pyridyl methanimine with bromopropionitrile as initiator and methyl ethyl ketone (MEK) as the solvent at room temperature. They found yields around 75% and experimental molecular weights 48% higher than the theoretical ones in spite of the PDI which was kept at 1.48. Krishnan et al. affirmed that the control of the ATRP polymerization of GMA was highly dependent on the solubility of the catalytic system in the reaction media. In that way, modification of the alkyl group over the ligand improved the solubility significantly. However, better polymerization control was observed in a bulk and diphenyl ether solution. Srinivasan reported no polymerization of GMA in nonpolar solvents and deviation from the theoretical molecular weight and slightly higher polydispersities when polar solvents were used at room temperature. There was also, a lack of reactivity when initiators, including chlorine as counterion, were used (18).

Cañamero et al. (19) reported the preparation of block copolymers of butyl acrylate from macroinitiators of polyglycidyl methacrylate (PGMA) with chloro end group. The PGMA-Cl macroinitiator was prepared by ATRP employing the catalytic system CuCl(I)/N,N,N',N'',N''-pentamethylethylenetriamine (PMDETA) and ethyl-2-bromo-isobutyrate as the initiator. In this case, PDI was around 1.50 at 50°C. Employing the same experimental conditions, Cañamero also reported the preparation of statistical copolymers of GMA and butyl acrylate (20).

In this study, we report the preparation of the random photochromic copolymer poly(glycidyl methacrylate-*r*-1'-(2-methacryloxyethyl)-6-nitro-3',3'-dimethylspiro-[2H-1]-benzopyran-2,2'-indoline) which can be used for the preparation of homogeneous films. When irradiated with ultraviolet light, it generates highly stable colored films, where this colored form can return to the colorless film when it is irradiated with a white light source. Such products can be useful in the integration of optoelectronic devices and eye lenses. Additionally, the presence of the oxirane ring provides these products with an enormous

versatility in coating applications. This work is one of the few examples reported in the literature where the spirobenzopyranindoline photochromic molecule is covalently bonded to a polymeric chain through a radically controlled polymerization technique. The optimization of all parameters involved in the controlled ATRP methodology ensures that the concentration of radicals should be low enough to sustain the integrity of the photochromic monomer and the oxirane ring.

2 Experimental

2.1 Chemicals

Glycidyl methacrylate (Aldrich 97%) was purified by distillation over magnesium sulfate; ethyl 2-methyl-2-bromopropionate (Aldrich) was distilled over calcium chloride; 2-butanone (methyl ethyl ketone MEK) (Aldrich 99%) was distilled over calcium chloride, copper (I) bromide was purified according to the reported method (21). Chloroform (J.T. Baker), N,N,N',N'',N''-pentamethyl diethylenetriamine (PMDETA), 2,2'-bipyridine (bipy), 1,1,4,7,10,10-hexamethyltriethyltetramine (HMTETA), Tetrahydrofuran (HPLC grade), and deuterated solvents were purchased from Aldrich and used without further purification.

2.2 Synthesis of the Photochromic Monomer, N-(2-Methacryloxyethyl)-3',3'-dimethylspiro-[2H-1]Benzopyrane-6-nitro-2, 2'-indoline

A mixture of 1.56 g (9.36 mmol) of 2-hydroxy-5-nitrobenzaldehyde, 3.14 g (9.36 mmol) of N-(2-methacryloxyethyl)-2,3,3-trimethylindolenine bromide, 2 mL (14.7 mmol) of triethylamine and 25 mL of distilled ethanol was placed in a three-neck round bottom flask and heated under reflux for 12 h. Then, the reaction mixture was rotoevaporated and the residue redissolved in 50 mL of chloroform and extracted with 20 mL of aqueous solution of 10% sodium hydroxide. The precipitate was recovered and washed with cold ethanol and then recrystallized in ethanol.

¹H-NMR (300 MHz, CDCl₃) δ: 8.05 (m, 2H), 7.45 (m, 2H), 7.15 (d, 1H, J = 7 Hz), 6.92 (d, 1H, J = 12Hz), 6.87(d, 1H, J = 7Hz), 6.79(d, 1H, J = 8Hz), 6.16(1H, J = 1.5Hz), 5.81 (d, 1H, 12Hz), 5.51(d, 1H, J = 1.5Hz), 4.54(t, 2H, J = 6.45Hz), 3.53(m, 2H), 1.96(s, 3H), 1.24(s, 3H), 1.17(s, 3H). ¹³C (50 MHz, CDCl₃) δ: 167.3, 159.53, 146.81, 141.25, 136.22, 135.85, 128.47, 128.03, 126.13, 122.95, 121.98, 120.12, 118.61, 115.75, 106.96, 62.90, 53.10, 42.73, 26.18, 20.17, 18.70. E.I.-M.S D.I.P. m/z, intensity,(%); 159(100), 420 (28). FT-IR (KBr Film) ν max 1718, 1518, 1163, 953, 746 cm⁻¹. Anal. Calcd. for C₂₄H₂₄N₂O₅: C, 68.6%; H 5.8%; N, 6.7%. Found: C, 68.58%; H, 5.93%; N, 6.41%. M.P. 184°C

2.3 General Procedure for the Homopolymerization of Glycidylmethacrylate by ATRP

A mixture of 0.0717 g (1 eq, 0.04998 mmol) of CuBr(I), 0.115 g (1 eq, 0.04998 mmol) of HMTETA, 7.09 g (100 eq, 0.04998 mol) of GMA, 6.7585 g of MEK as solvent and 0.0969 g (1 eq, 0.04998 mmol) of ethyl 2-methyl-2-bromopropionate was placed in a Schlenk test tube under inert atmosphere. The reaction mixture was frozen and evacuated in liquid nitrogen temperature to remove the dissolved oxygen. After reaching room temperature, the reaction mixture was then heated to 50°C. When the reaction time was attained, the content of the test tube was dissolved in THF and precipitated in hexanes. Finally the solid was filtrated and vacuum dried.

2.4 General Procedure for ATRP Copolymerization of Glycidylmethacrylate and 2-Methacryloxyethyl-6-nitro-3',3'-dimethylspiro-[2H-1]-benzopyran-2,2'-indoline

A mixture of 0.0126 g (1 eq, 0.127 mmol) of CuBr(I), 0.0293 g (1.0 eq, 0.127 mmol) of HMTETA, 1.355 g (75 eq, 9.54 mmol) of GMA, 1.3307 g of 2-methacryloxyethyl-6-nitro-3',3'-dimethylspiro-[2H-1]-benzopyran-2,2'-indoline (25 eq, 3.168 mmol), 6.7585 g of MEK as solvent and 0.0246 g (1 eq, 0.127 mmol) of ethyl 2-methyl-2-bromo-propionate was placed in a Schlenk test tube under inert atmosphere. The reaction mixture was frozen and evacuated in liquid nitrogen temperature. After reaching the room temperature, the reaction mixture was then heated to 50°C. When the reaction time was attained, the content was dissolved in THF and precipitated in hexanes, the solid was filtrated and vacuum dried.

2.5 Kinetic Studies

From a reaction mixture prepared as previously described, several aliquots were taken and placed in five ignition tubes. Each tube was frozen in liquid nitrogen, evacuated and sealed with the appropriate device. The reaction mixture was heated to 50°C and once the estimated reaction time was attained for each tube, the ampoule was broken, its content dissolved in THF and precipitated in hexanes. The polymer was then filtered and vacuum dried.

2.6 General Procedure to Evaluate the Reactivity Ratios by the Extended Method Kelen-tüdös for the Copolymerization of Glycidylmethacrylate and the Photochromic Monomer

Six experiments were carried out according to the general procedure of ATRP. For each, the molar ratio between GMA and the photochromic monomer was fixed from 15 to 80 molar % of the photochromic monomer. Samples were placed in ignition tubes, frozen, evacuated, sealed and

maintained at 50°. For each 20 min of reaction, one ampoule was removed from the oil heating bath, broken, and its content dissolved in THF, and then precipitated in hexanes. The residue was filtered and vacuum dried. All samples were analyzed by ¹H-NMR.

2.7 Measurements and Analysis

The characterization of related compounds was determined by a NMR (200 MHz) spectrophotometer Varian Gemini 2000. Chemical shifts were expressed in parts per million from 0 to 10 ppm. Tetramethylsilane (TMS) was used as internal standard. FT-IR spectra were taken with a Nicolet Magna 550 Infrared spectrophotometer. The polymers obtained were characterized by a HPLC Hewlett Packard 1100 series equipped with both refractive index and ultraviolet (254 nm) array detectors using THF HPLC grade as the solvent at the flow rate of 1 mL/min at 30°C. The molecular weight and polydispersity values were determined by the size exclusion chromatography (SEC) using polystyrene columns (styrogel 10⁵, 10⁴, 10² ?) and polymethylmethacrylate standards with molecular weight in the range of 162 to 6,300,000 g/mol. Conversion of PGMA and the copolymer poly(glycidyl methacrylate)-*r*-1'-(2-methacryloxyethyl)-6-nitro-3',3'-dimethylspiro-[2H-1]-benzopyran-2,2'-indoline were determined by gravimetric analysis. The composition of the copolymers was calculated by NMR according to the integration of the two hydrogen atoms at positions 5 and 7 of the photochromic (23) moiety that appeared at 8.05 ppm and the three hydrogen atoms of the glycidyl fraction at 4.1, 3.6 and 3.0 ppm. Theoretical numeral molecular weights (M_n) of the homopolymers were calculated with the following equation:

$$M_{n\text{theoretical}} = (M_{w\text{monomer}})[M]_o \text{Conversion}/[I]_o$$

Where $M_{w\text{monomer}}$ is the molar mass of the monomer and is equal to 142 g/mol, $[M]_o$ represents the initial monomer concentration and $[I]_o$ the initiator concentration.

In addition, M_n of the copolymers was calculated with the following equation:

$$M_{n\text{theoretical}} = (M_{w\text{monomer}1})([M_1]_o \text{Conversion})/[I]_o + (M_{w\text{monomer}2})([M_2]_o \text{Conversion})/[I]_o$$

Where $M_{w\text{monomer}1}$ is the molar mass of the GMA and is equal to 142 g/mol, $[M_1]_o$ represents the initial monomer concentration of GMA, $M_{w\text{monomer}2}$ is the molar mass of the photochromic monomer and is equal to 420 g/mol, $[M_2]_o$ represents the initial concentration of photochromic monomer and I_o the initiator concentration.

All the copolymers obtained were purified on a first attempt by precipitation on hexanes. The polymer obtained was then again dissolved in chloroform and passed through a column packed with neutral aluminum oxide. Finally, the

solution was again precipitated twice on hexanes, filtered, dried, and the polymer recovered.

3 Results and Discussion

3.1 Homopolymerization of GMA

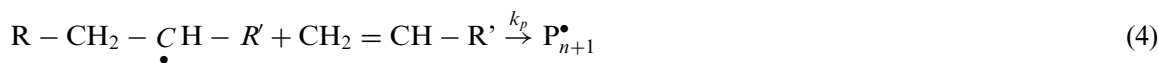
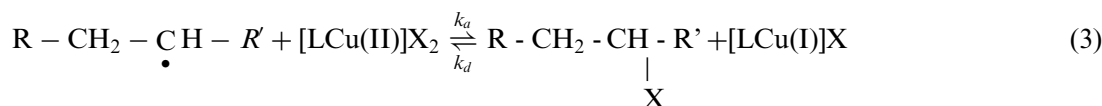
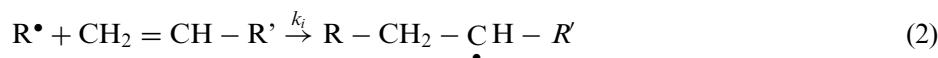
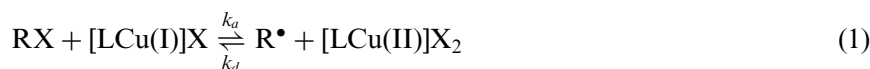
ATRP is a controlled polymerization method which offers great opportunity to manipulate reactive and sensible monomers mainly due to the low concentration of radicals derived during polymerization from the rapid equilibrium between the growing radicals and the dormant species generated by the metallic complex. According to the literature, the methacrylic monomers can be polymerized by the catalysis of complexes prepared from copper (I) salts and nitrogenated bases (18). These complexes are generated by the interaction of the non-bonding electrons on the nitrogen atom and the *d* atomic orbitals in the copper (I) atom. The interaction modifies the ability of the copper atom to donate or accept an electron, which is commonly provided by the atom of halogen from the initiator. The ATRP process involves four steps. The first is the initiation of the interaction between the copper (I) complex and the alkyl halide molecule. This initiation step results in a homolytic dissociation generating an alkyl free radical and a halogen radical, the latter is then reduced to a halide and the copper atom from the complex oxidized to Cu(II) expanding its coordination sphere (Equation 1 in Scheme 1). Propagation is the second step, where the alkyl free radical reacts with one vinyl monomer molecule to set off the polymerization process (Equation 4). Deactivation, the third step, then follows, as the free radical generated during propagation reacts with the halogen free radical which is derived from the reduction of the copper complex and the oxidation of the halide atom. During this process, the radicals are deactivated and the “dormant species” are formed (Equation 3).

Termination is the final fourth step, consisting mainly of two termination paths. The first path is the collision between two growing radicals and is named recombination of radicals (Equation 5) and the second path occurs after the subtraction of the hydrogen atom in the growing radical generating a vinyl compound (Equation 6).

Ideally, the propagation and deactivation steps in ATRP can be repeated indefinitely until all the monomers have been consumed. These two steps would produce a low concentration of active radicals during polymerization and therefore, would minimize the termination step. However, in practice, an efficient and fast initiation is favored in order to avoid undesirable reactions. With an inefficient initiation, the concentration of copper (II) is low and would cause the incapability to deactivate the free radicals, resulting in the termination by disproportionation and the presence of coupling reactions causing the polymerization to go out of control. In order to keep the system in control, an efficient initiation, a proper oxidation-reduction potential of the copper complex and homogeneous solution during the entire polymerization are essential.

In order to ensure the good control on the polymerization and less impact on the oxirane ring and the photochromic monomer, it is very important to have the appropriate selection of the parameters such as solvent, nitrogenated base, alkyl halide (type of halogen in the initiator) and temperature.

The first approach in this study was to find well-controlled conditions for ATRP during the random copolymerization of GMA and the photochromic monomer. The homopolymerization of the GMA was selected as a model for this purpose. The suitable solvent for such homopolymerization was selected between toluene and 2-butanone (MEK). The experimental conditions employed include an amine copper complex consisting of 2,2'-bipyridine (bipy) and CuBr, allyl bromide as initiator and GMA in a molar ratio of 3:1:1:100, respectively. For both solvents, the



Sch. 1. Accepted mechanism for the ATRP polymerization.

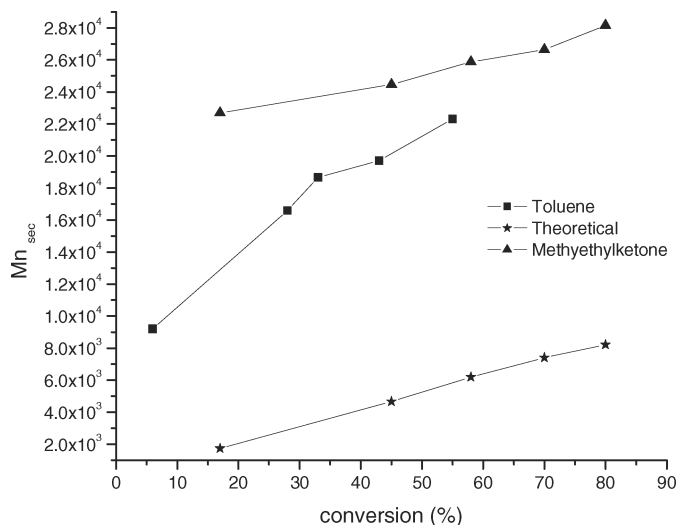


Fig. 1. Molecular weight vs. conversion for the homopolymerization of GMA in toluene and MEK as solvents.

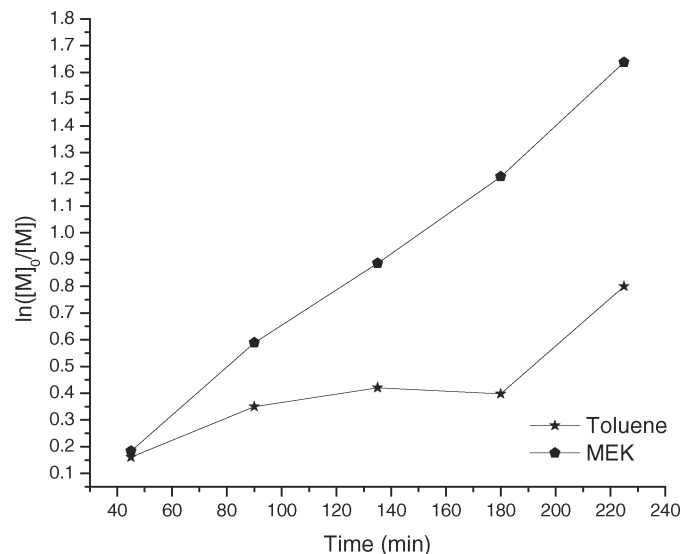


Fig. 2. Semi-logarithmic kinetic plot behavior for the homopolymerization of GMA in toluene and MEK as solvents.

cooper complexes were soluble during the complete polymerization process. After experiments at 50°C, it was found that in 225 min of reaction, the reaction reaches 55% of polymer yield when it was carried out in toluene and 78% of polymer yield with MEK at the same temperature and time. When the results for MEK polymerizations ($M_n = 27,000$ gr/mol, $PDI = 1.68$) were analyzed, a 3-fold increase for the practical over the theoretical molecular weight was observed, while for toluene ($M_n = 22,500$, $PDI = 1.96$), there was a 4.5-fold increase. In spite of these results, an almost linear relationship was found between molecular weight and conversion as shown in Figure 1.

Concerning the kinetic behavior of the polymerization in both solvents, a first order model was established by graphing $\ln([M]_0/[M])$ vs. time as shown in Figure 2.

Due to the linearity found in the semi-logarithmic curves, it could be assumed that the concentration of radicals was constant when MEK was used as the solvent. The loss of control during polymerization was due to the low efficiency of the initiation process where there existed an inefficient reaction between the complex $Cu(bipy)_2$ and the initiator allyl bromide. This lack of reactivity was attributed to the change in the original molecular ratio ($[M]_0/[I]_0$). In this case, the polymer chain should be growing from the dormant species instead of from the original alkyl halide molecule due to the lower bond energy for PGMA-Br than for the allyl bromide molecule (24). The result is a higher molecular weight when compared with the theoretical one. By comparing the results obtained from MEK with those obtained from toluene, it was clear that not only the previously described parameters had affected polymerization, but also poor solubility of the complex was a factor as well, as confirmed by the poor linearity of the semi logarithmic graph.

MEK was selected as the solvent for further experiments based on the encouraging results. The results also confirmed that reactivity of the initiation step must be increased. This was done by using ethyl 2-bromo-2-methyl propionate as initiator to evaluate its ability to develop a good reaction system with the copper (I) complex and a bidentate amine such as 2,2'-bipyridine (bipy) or a multi-dentate amine such as PMDETA and HMTETA. In a previously reported work for the polymerization of methacrylic monomers by ATRP^[25], it was described that the molar ratio between copper:amine to prepare the complex must be adjusted. Experimentally, for multidentate amines, a molar ratio of 1:1 was used, while for bidentate amines the established ratio was 1:3. The monomer:initiator molar ratio used was 100:1.

In the semi-logarithmic curve in Figure 3, the polymerization where HMTETA was employed, shows linear behavior with an apparent polymerization constant (K_{app}) equal to $13.67 \times 10^3 \text{ min}^{-1}$, confirming the existence of control over polymerization. A similar result is found for bipy with $K_{app} = 11.94 \times 10^3 \text{ min}^{-1}$, however, a small deviation from the linearity was seen. The ligand with the smallest K_{app} of $2.54 \times 10^3 \text{ min}^{-1}$ is PMDETA. By using this ligand, the polymerization of GMA only reaches 37% of polymer yield in 225 reaction min in contrast to 90% and 92% yielded for HMTETA and bipy, respectively.

Because the kinetic results of bipy and HMTETA were quite similar, it was decided to use HMTETA in further experiments, mostly for its better control over the molecular weight ($M_{n,exp} = 7351$ g/mol, $PDI = 1.57$). This result shows that the correlation between theoretical and experimental molecular weights had only a 0.8-fold increase for HMTETA, instead of the 3-fold increase previously obtained for bipy. The NMR characterization of the polymer

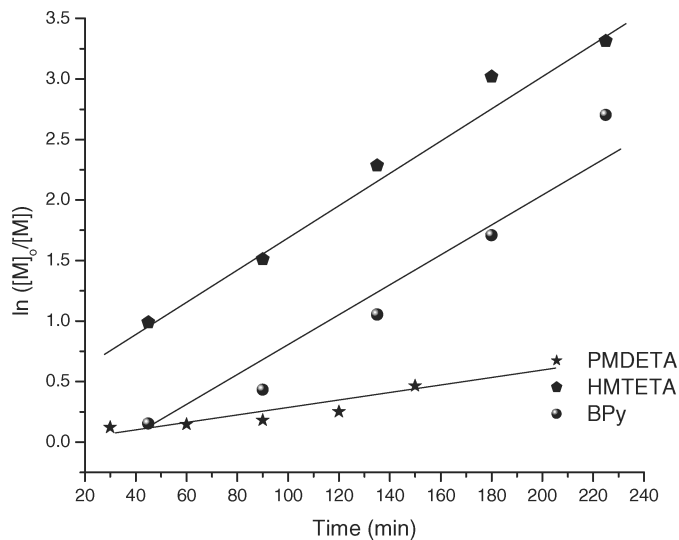


Fig. 3. Semi-logarithmic kinetic plot for the homopolymerization of GMA by using PMDETA, HMTETA and BiPy as ligands.

prepared clearly showed that the oxirane ring remained unchanged as could be seen in the unequivocal signals of the ^1H spectra. The couple of diastereotopic hydrogens in the methylene from the glycidyl group appeared as a complex group of signals with chemical shifts of 4.45 and 3.89 ppm, in addition to the three signals of the oxirane ring with chemical shifts of 3.25, 2.93 and 2.78 ppm.

3.2 Copolymerization of GMA and 1'-(2-Methacryloxyethyl)-6-nitro-3',3'-dimethylspiro-[2H-1]-benzopyran-2,2'-indoline

Once the reaction conditions for the living controlled polymerization of GMA were established, the random copolymerization of GMA and 1'-(2-methacryloxyethyl)-6-

nitro-3',3'-dimethylspiro-[2H-1]-benzopyran-2,2'-indoline was performed using the 15% by weight of the photochromic monomer (Figure 4).

The photochromic monomer was prepared according to a previously reported method (22). The methacrylic moiety was introduced through the heterogeneous reaction between the N-(hydroxyethyl)-2,3,3-trimethylindolenonium bromide and methacryloyl chloride in a polar solvent. The esterified salt was easily purified by crystallization in chloroform-hexane. Further condensation with 5-nitro-2-hydroxybenzaldehyde produced the photochromic monomer in high yield. This monomer was able to respond to the ultraviolet light, generating a colored molecule which could revert to its colorless state with white light or temperature.

The selected catalytic system for the copolymerization reaction comprised of HMTETA as ligand, CuBr(I), and methyl-2-bromo-2-methylpropionate at 50°C in a molar ratio of 1:1:1:100 as employed in the homopolymerization of GMA. After 50 min of reaction, the system yielded 75% of the copolymer which was recovered and purified by column chromatography packed with neutral aluminum oxide and chloroform as the mobile phase, followed by precipitation in hexanes.

The copolymer was analyzed by gel permeation chromatography using both detectors: UV and refractive index. By UV (at 254 nm) detection, the photochromic monomer could be easily detected because of its highly conjugated structure, while by the refractive index detector, both fractions in the copolymer, GMA and the photochromic could be detected.

The normal distribution elution curves in Figure 5 are possibly a confirmation that the copolymer composition is homogeneous.

This can be deduced from the fact that the eluted macromolecules contain both co-monomers where only the photochromic monomer can absorb UV light. This observation

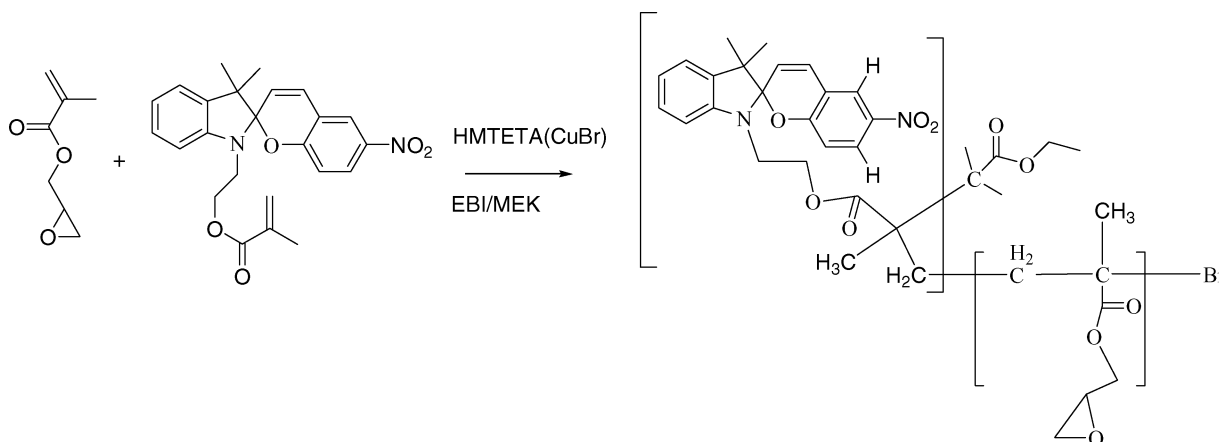


Fig. 4. Preparation of the Poly(glycidyl methacrylate-*r*-1'-(2-methacryloxyethyl)-6-nitro-3',3'-dimethylspiro-[2H-1]-benzopyran-2,2'-indoline) by ATRP.

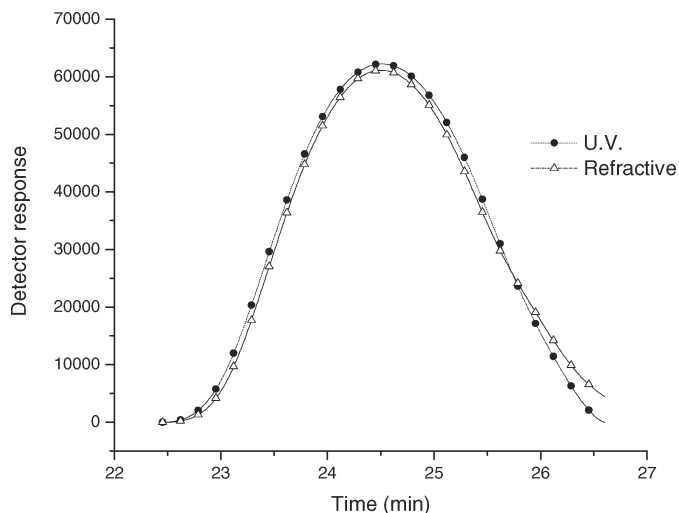


Fig. 5. Elution curve for the GPC analysis of the random copolymer with the dual array detectors.

confirms the existence of random copolymers. The molecular weight calculated using PMMA standards was $Mn_{exp} = 8598$ g/mol ($Mn_{theo} = 9052$ g/mol) and $PDI = 1.45$.

The characterization was completed when the 1H -NMR spectra (Figure 6) show the **a** and **a'** aromatic hydrogen atoms at 8.00 ppm, (23) and the aromatic five hydrogen atoms between 7.45 and 6.68 ppm, which correspond to the photochromic monomer. Additionally, the methylene hydrogen atoms from the glycidyl group show chemical shifts of 4.45 and 4.18 ppm. Finally, the three hydrogen atoms from the oxirane ring can be detected with chemical shifts of 3.25, 2.93 and 2.78. The composition of this

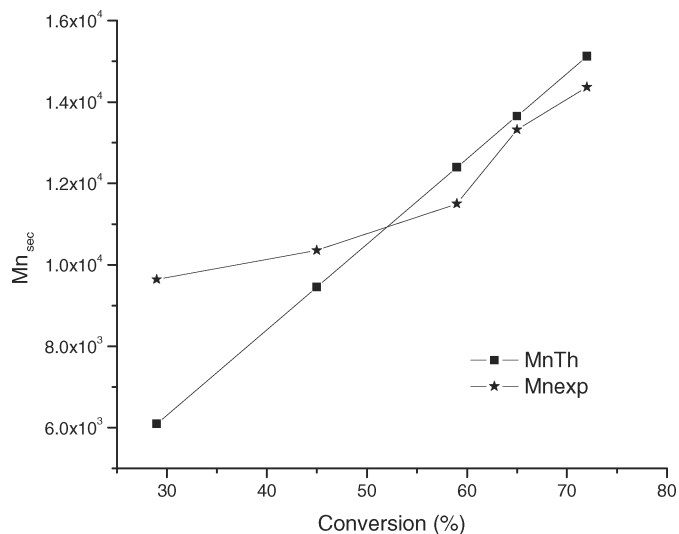


Fig. 7. Molecular weight dependence of the random copolymerization of GMA and the photochromic monomer as a function of the monomer conversion.

copolymer was determined by the relationship between the integrals of the two hydrogen atoms with chemical shift of 8.0 ppm which corresponds to the photochromic monomer and the three hydrogen atoms at 3.25, 2.93 and 2.78 ppm of the oxirane ring.

The kinetic study provides evidence of the living character of this copolymerization as confirmed by the linear dependence between molecular weight and the conversion of monomers (Figure 7).

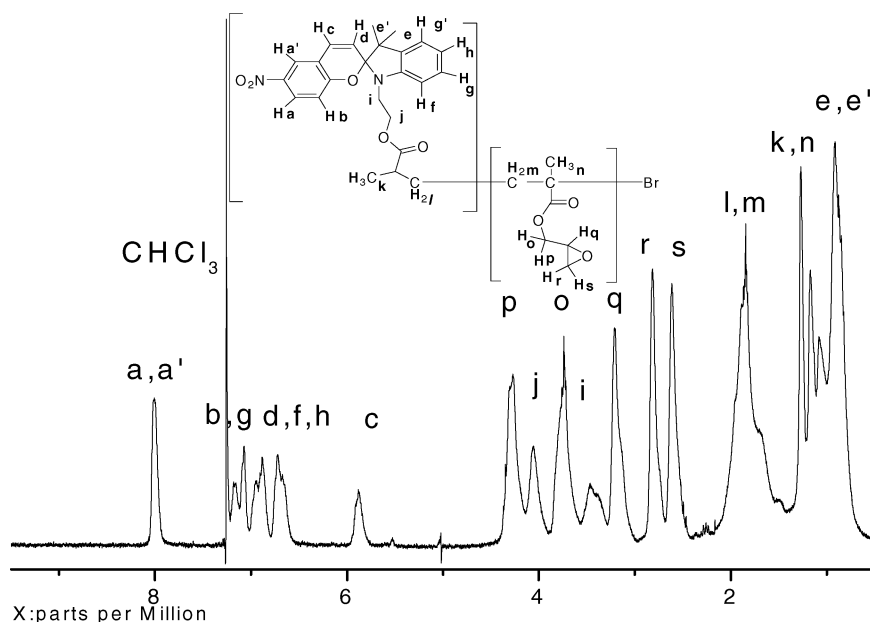


Fig. 6. 1H -NMR for the copolymer of GMA-*r*-1'-(2-methacryloxyethyl)-6-nitro-3',3'-dimethylspiro-[2H-1]-benzopyran-2,2'-indoline, with 18.5% molar content of the photochromic monomer (40% by weight).

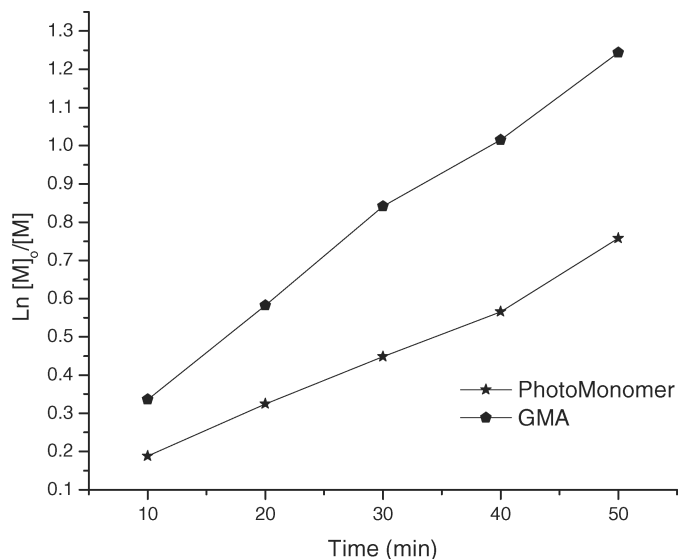


Fig. 8. Semi-logarithmic kinetic plot for the copolymerization of GMA and 1'-(2-methacryloxyethyl)-6-nitro-3',3'-dimethylspiro-[2H-1]-benzopyran-2,2'-indoline.

It is also necessary to evaluate the apparent rate constant of polymerization for each comonomer and the copolymer composition by NMR. The semi-logarithmic curve (Figure 8) shows clear evidence of the living character of the copolymerization and similarity of the polymerization rates of the used monomers. After calculations, K_{app} for GMA is found to be $22.46 \times 10^3 \text{ min}^{-1}$ and $13.79 \times 10^3 \text{ min}^{-1}$ for the photochromic monomer. With this small difference in the rate constant values, it is possible to assume that a random copolymer was prepared.

When a 300 ppm solution in THF of the copolymer poly(GMA-*r*-1'-(2-methacryloxy ethyl)-6-nitro-3',3'-dimethylspiro-[2H-1]-benzopyran-2,2'-indoline) was placed in a quartz cuvette, irradiated for 500 milliseconds with a U.V. lamp, a clear deep blue colored solution appeared which absorbed in the visible region at 590 nm as can be seen in Figure 9.

3.3 Determination of the Monomer Reactivity Ratio of GMA and 1'-(2-Methacryloxy ethyl)-6-nitro-3',3'-dimethylspiro-[2H-1]-benzopyran-2,2'-indoline

It is important to mention that a controlled living polymerization offers a better possibility for the preparation of copolymers with well defined structures than the conventional radical polymerization methods. This premise is based on the fact that the concentration of active radicals in ATRP is significantly lower during the propagation step and all polymer chains can grow simultaneously with the same chemical composition. However, changes during this radical polymerization process result in heterogeneous composition depending on the ability of the homo propagation (k_{11} or k_{22}) and cross propagation (k_{12}) of

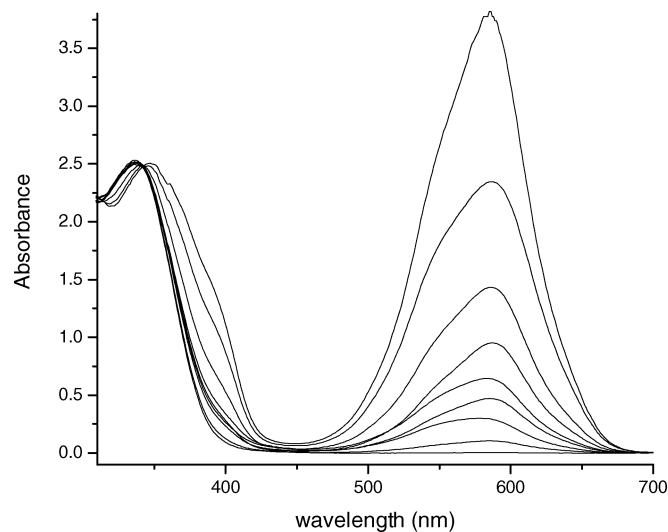


Fig. 9. Visible-ultraviolet spectra of GMA-*r*-1'-(2-methacryloxyethyl)-6-nitro-3',3'-dimethylspiro-[2H-1]-benzopyran-2,2'-indoline, 300 ppm solution in tetrahydrofuran, the copolymer content has a 18.5% molar of the photochromic monomer (40% by weight). This solution was irradiated with UV light and the spectra were taken after every 100 milliseconds.

each comonomer, which determines the structure of the copolymer.

The monomer reactivity ratios were obtained by the extended Kelen-Tüdös equation from the copolymer composition calculated by NMR for copolymers prepared with conversions between 40 to 50% (26). According to the extended Kelen-Tüdös method, the variation between the monomer feed composition and conversion is considered. The monomer and copolymer compositions obtained by $^1\text{H-NMR}$ are described in Table 1.

From the Kelen-Tüdös equation (Figure 10), the monomer reactivity ratio is estimated for GMA $r_{GMA} = 0.985$ and for the photochromic monomer, $r_{PHM} = 0.596$.

According to these values, it is possible to assume that GMA has the same tendency toward the homo propagation than to the cross propagation, since this value is almost 1, making $k_{GMA} = k_{11}/k_{12} \approx$ then $k_{11} \approx k_{12}$. In

Table 1. Photochromic and GMA molar fraction in the feed ($f_{\text{photomonomer}}$ and f_{GMA} respectively), conversion and copolymer composition for the copolymerization obtained by ATRP.

Exp.	f_{GMA}	$f_{\text{Photomonomer}}$	r	Conversion (%)	
				F_{GMA}	$F_{\text{Photomonomer}}$
1	0.859	0.141	44	0.884	0.116
2	0.763	0.237	41	0.710	0.290
3	0.693	0.307	50	0.668	0.332
4	0.563	0.437	51	0.573	0.427
5	0.212	0.788	41	0.261	0.739
6	0.135	0.865	40	0.236	0.764

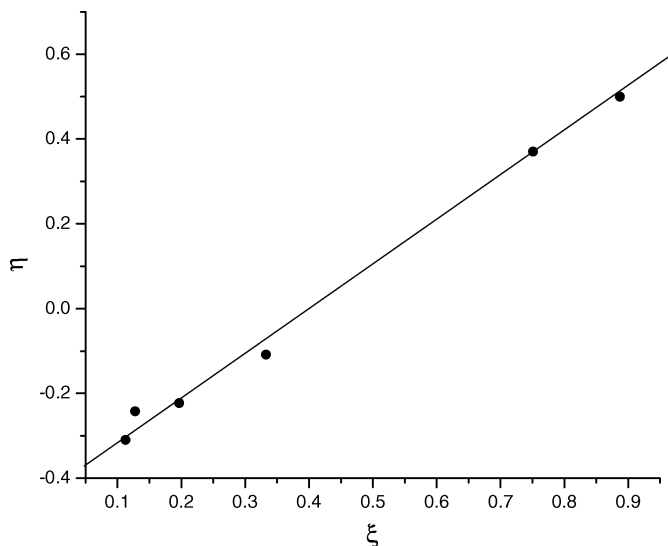


Fig. 10. Extended Kelen-Tüdös, method for the determination of the reactivity ratios of GMA and 1'-(2-methacryloxyethyl)-6-nitro-3',3'-dimethylspiro-[2H-1]-benzopyran-2,2'-indoline.

contrast, the photochromic monomer has more tendency to the cross propagation than to the homo propagation from $k_{PHM} = k_{22}/k_{12} < 1$ meaning that $k_{22} < k_{12}$. This observation could be logical since the vinyl fraction of the photochromic monomer has a voluminous substituent group and the steric hindrance could be responsible for its smaller reactivity.

4 Conclusions

The conditions for living radical homopolymerization of GMA were established using the catalytic system comprising of HMTETA, CuBr(I), ethyl 2-bromo-2-methyl propanoate in MEK as the solvent, at 50°C. By employing this system, the oxirane ring was kept intact and the polymers obtained showed good correlation with the theoretical molecular weight and also had a low PDI index. The copolymerization reaction of GMA with the photochromic monomer was successful under the ATRP conditions and the apparent rate constant of polymerization for both monomers was quite similar. The determination of the monomer reactivity ratio provided clear evidence of the preference of the photochromic monomer for the cross propagation. The prepared photochromic copolymer retained the oxirane functionality and also the ability to perform reversible photochemical activity, making this macromolecule ideal for technological and academic applications.

Acknowledgements

The authors are grateful to the Mexican Council of Science and Technology (CONACYT) for financial support through the project number 53186, to Lourdes Guillen

Jose Guadalupe Telles and Julieta Sanchez for their helpful collaboration during the characterization of the reported molecules, and also to M. C. Sion NG from the Peace Corps for his valuable collaboration.

References

- Woodworth, B.E., Coca, S. and O'Dwyer, J.B. U.S. Patent 6,441,066 2002, *Chem. Abstr.*, (2002) 137, 186369.
- Barkac, K.A., Coca, S., Franks, J.R., Humbert, K.A., Lamers, P.H., Martin, R.L., O'Dwyer, J.B., Olson, K.G. and White, D. PCT Int. Appl A1 20000309, WO 2000012583, 2000, *Chem. Abstr.*, (2000) 132, 195898.
- Teare, D.O., Barwick, D.C., Schofield, W.C.E., Garrod, R.P., Ward, L.J. and Badyal, J.P.S. (2005) *Langmuir*, 21(24): 11425–11430.
- Samadi, A., Husson, S.M., Liu, Y., Luzinov I. and Kilbey, S.M. (2005) *Macromol. Rapid Commun.*, 26(23), 1829–1834.
- Ramakrishnan, A., Dhamodharan, R. and Ruehe, J. (2006) *Journal of Polym. Sci. Part A: Polym. Chem.*, 44(5), 1758–1769.
- Li, G., Zhu, X., Zhu, J., Cheng, Z. and Zhang, W. (2005) *Polymer*, 46(26), 12716–12721.
- Biacak, N., Gazi, M., Galli, G. and Cjellini, E., (2006) *Journal of Polym. Sci. Part A: Polym. Chem.*, 44(23), 6708–6716.
- Crano, J.C. and Giglielmetti, R.J. *Organic Photochromic and Thermochromic Compounds*, Plenum Press: New York, Vol. 2, 10–32, 1999.
- Ota, H., Imizu, T. and Shinde, K. PCT Int. Appl A1 20070322 WO 2007032127, 2007, *Chem. Abstr.* (2007), 146, 339716.
- Katsuhiro, M., Junji, T. and Naoto, T. PCT Int. Appl A1 20040916 WO 2004078364, 2004, *Chem. Abstr.* (2004), 41, 261638.
- Komuro, Y. and Momoda, J. PCT Int. Appl A1 20020221 WO 2002014387 (2002) *Chem. Abstr.* (2002), 136, 185037.
- Valette, L., Massardier, V., Pascault, J-P. and Magny, B. (2002) *J. Appl. Polym. Sci.*, 86(3), 753–763.
- Lutz, J.F., Neugebauer, D. and Matyjaszewski, K. (2003) *J. Am. Chem. Soc.*, 125(23), 6986–6993.
- Ray, B., Isobe, Y. and Sawamoto, M. (2004) *Macromolecules* 37(5), 1702–1710.
- Lutz, J.F., Jakubowski, W. and Matyjaszewski, K. (2004) *Macromol. Rapid Commun.*, 25(3), 486–492.
- Matyjaszewski, K., Coca, S. and Jasiczek, C.B. (1997) *Macromol. Chem. Phys.*, 198(12), 4001–4009.
- Krishnan, R. and Srinivasan, K.S.V. (2003) *Macromolecules*, 36(6), 1769–1771.
- Krishnan, R. and Srinivasan, K.S.V. (2004) *Macromolecules*, 37(10), 3614–3622.
- Camareño, P.F., De la Fuente, J.L., Madruga, E. and Fernández-García, M. (2004) *Macromol. Chem. Phys.*, 205(16), 2221–2228.
- De la Fuente, J.L., Camareño, P.F. and Fernández-García, M. (2006) *J. Polym. Sci. Part A: Polym. Chem.*, 44(6), 1807–1816.
- Karanam, A., Goossens, H., Klumperman, B. and Lemstra, P. (2003) *Macromolecules*, 36(22), 8304–8311.
- Elizalde, L.E., Ledezma, R. and Lopez, R.G. (2005) *Synthetic Communications*, 35(4), 603–610.
- To the referring assignation please review McArdle, C.B. (Ed.) "Applied Photochromic Polymer Systems" 1st Edition, Blackie: England, 32, 1992.
- Matyjaszewski, K., Shipp, D.A., Wang, J. L. and Grimaud, T. (1998) *Macromolecules*, 31(20), 6836–6840.
- de los Santos, G., Elizalde, L.E., Castro, B., Garcia, A.E. and Medellín, D.I. (2004) *Revista de la Sociedad Química de México*, 48(4), 332–337.
- Tüdös, F. and Kelen, H. (1981) *Journal of Macromolecular Science. Chemistry*, 16(7), 1238–1297