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Synthesis of block copolymers consisting of liquid crystalline and amorphous segments by living/controlled radical polymerization

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Summary

Living polymerization is most often observed in systems where the growing species are ions. In such systems the chain ends do not react to each other due to elestrostactic repulsion, but only to monomers allowing, this way, the control in structure of the formed polymer. Free radicals, which are the growing species in the radical polymerization, easely undergo combination and prevent a living radical polymerization. Thus, a great challenge to polymer science was in meeting a system that offered to the radical polymerization a radical stabillization alike in ionic polymerizations. At the same time, the radicals should undergo rapid propagation and should not be able to initiate new chains, in a controlled reaction. Some succesfull techniques of living/controlled radical polymerization, such as stable free radical polymerization (SFRP), mediated by nitroxide, INIFERTER and atom transfer polymerization (ATRP) will be overviewed here, as well as their application to the synthesis of liquid crystalline polymers.

Introduction

Block copolymers consisting of amorphous and liquid crystalline (LC) segments are systems that can originate a vast number of possible combinations of properties and structures. These materials are of interest due to the simultaneous emergence of two ordering phenomena: the self-orientation of the mesogens, that takes to an ordered structure of the LC block and the phase separation of the block copolymer. [1] These characteristics allow the use of these products as compatibilizers to mixtures of polymers with LC components for new materials with properties directed for special applications, as for instance, electro-optical properties. In the study of such systems it is of great importance that the polymerization reaction proceeds in a controlled way, therefore the molar mass and its distribution control the size and the type of LC microphases.

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The use of living techniques for the polymerization of side-chain liquid-crystalline polymers offers the possibility to obtain resins with well defined structures and control of the chain size. Living systems such as anionic [2] and cationic [3] were successfully used in that sense. These techniques, however, have their industrial application limited by the need of high purity of monomers and solvents and for being highly selective for certain types of monomers.

The polymerization through free radicals can be applied to any monomer that reacts by an addition mechanism, being less sensitive to system impurities and of easy execution, allowing the use of the processes in solution and suspension. Those advantages justify the preference that this technique has over ionic techniques as industrial process of polymerization. [4] On the other hand, in a typical free radical process, the propagating chains can suffer chain transfer reactions, besides premature termination, taking to polymers with broad molar mass distribution (MMD). These factors hinder the control of the physical properties of the resin and the construction of a complex architecture.

Some living/controlled radical polymerization techniques

The growing need to obtain new materials for specific uses and with great performance demands, led to the search for new ways for obtaining the control of the physical properties and of the architecture of the polymers increased so much that resulted in a great effort in the goal of combining the attributes of the living systems with the economical advantages of the radical polymerization.

The first technique investigated that presented some positive results in this sense was the one so-called INIFERTER, where an alkyl-thyuram disulfide was used to initiate the polymerization and, at the same time, reversibly terminate the growing chains in a cycle that is repeated until all monomer is consumed. [5] Although the system showed some limitations in its applications due to low propagation rates, to ease in initiating new chains during the reaction and to lost of activity of the INIFERTER fragment, [6] it was used to prepare block and graft copolymers by photo or thermal methods with some controlled characteristics.

In 1995, independently from each other, Sawamoto et all.[7] and Wang & Matyjaszewski [8] reported the discovery of novel kind of “living” free radical polymerization. Sawamoto reported “living” radical polymerization of methyl methacrylate initiated by

$CCl_4/RuCl_2(PPh_3)_2/MeAl(ODBP)_2$, while Matyjaszewsky announced the polymeryzation of styrene initiated by alkyl halides/CuCl/bipyridine. Both methods were made by analogy with well-established metal catalyzed halogen atom addition (ATRA) of alkyl halides to alkenes. [9] The formers called their novel polymerization reaction "Atom Transfer Radical Polymerization" and the mechanisms proceeds as ATRA mechanisms.

At the same year, Percec & Barboiu [10] reported that the use of arenesulphonyl chloride instead of alkyl halides is usefull to be used as initiator in the ATRP technique. The electrophilic sulfonyl radicals add reversible and selectively to nucleophilic alkenes.

In 1998 was discovered by Matyjaszewski's groups that the halides exchange (Cl and Br) in ATRP technique gives the fastest initiation rate relative to propagation rate, which is a pre-requesite for controlled polymerization and it is more critical for MMA than styrene polymerization. [11]

Although is possible to use many different kind of catalyst in the ATRP technique the principal system used is based on copper. Other polymerizations were studied by this system, such as homopolymerization of differents kinds of high acrylates [12], functional acrylates, [13] acrylonitrile, [14] functionalized styrene, [15] 4-vinylpyridine [16] and 2-(dimethylamino)ethyl methacrylate [17.]

Pugh & Chang [18] first reported the use of ATRP to obtain liquid crystalline polymer. They pointed that this technique is usefull because polymers with narrow LC transitions could be obtained, probably due the to narrow MMD, when compared with a conventional free radical technique. They claimed that the broadness of the transitions could be produced by transfer reaction inherent to free radical reaction during the polymerization

Rizzardo and Solomon [19] first reported the use of alkoxyamine initiators in the preparation of oligomers of acrylates and methacrylates with some controlled characteristics, which were verified only at very low conversion.

The technique presented by Georges et al. in 1993 [20] met the goal of minimize termination by radical coupling and allow the control of end-group structure. It was based on the use of a stable free radical, in this case, the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to reversibly end-cap the growing chain. Being more stable than the INIFERTER fragment it permitted the reaction to proceed at higher rates and in a living fashion. In this work, where a mixture of monomer, initiator and TEMPO was heated above 100° C, were obtained polystyrene resins with

MMD values comparable to those of anionic process and below the theoretical limit for conventional free radical polymerization (1.5). Since then, an explosive development has been experienced in this field and an increasing number of works were reported, involving new reaction conditions and techniques, additives for rate enhancement, use of new stable radicals replacing TEMPO and synthesis of other polymers than polystyrene and of block and graft copolymers.

The pioneer work carried out by Georges et al. found still a lack to its large application because the resins produced showed a low molar mass and the time reaction for high conversion was too long. The same research group worked on the use of strong organic acids, such as canphorsulfonic acid [21] and organic acid salts [22] to rate enhance the styrene polymerization. This way, a conversion of 90%, which was initially achieved only in 69 hours, was reached in 4 hours, with a molar mass of 18000 instead of the 8000 first found. The MMD, although increased to over 1.30.

Also the use of acylating agents was investigated, being found that the addition of 1 weight percent of acetic anhydride leads to a reaction time of 4 hours and, this way, permitting a greater control over the polymerization process and the obtention of resins with molar masses up to 150000. [23]

The mechanism to living radical polymerization mediated by nitroxide involves the reversible termination of growing radicals by this nitroxide, in a bimolecular reaction. Besides acting in the promoted decomposition of the initiator, the scavenger radical must have a low bond dissociation enthalpy, in order to permit the propagation and an endothermic enthalpy to styrene reaction not to initiate new chains and keep low MMD. This thermodynamic features aids in the choice of the nitroxide structure and was carried out by Kazmaier et al. [24], confirming the utility of TEMPO radical on this technique. Even so, other nitroxides have been experimented and claimed to be more actives than TEMPO. Typical examples of these nitroxides are those based on imidazolidinone structure [13] and on N-allyl-TEMPO structures. [25] The effect of the acidic media in the kinetic of polymerization was also confirmed by the use of a TEMPO radical substituted with phosphonoxy group. [26]

The major studies that proved succesfull on nitroxide mediated polymerization involved synthesis of polystyrene and its derivatives. The extension of this technique to the preparation of acrylates and dienes has always shown itself to be troublesome. It happens because these systems are more affected by the nitroxide concentration during the course of the reaction. Some studies pointed to an increase of the nitroxide levels in the acrylate polymerization up to a moment when they act as an inhibitor preventing the chain growth.[27]

Two routes were investigated to undertake this problem. The first one was based on the use of macroinitiators to certify that nitroxide concentration would be kept in a level just enough to control the monomer addition.[28, 29] By this method n- butyl acrylate was polymerized to yield resins with M_n = 12000 in 4.5 hours. Another way of balancing the amount of free nitroxide in the reaction was done by adding a radical scavenger, in this case, reducing sugars to react with the excess of nitroxide and allow the propagation. Here were obtained poly(n-butyl acrylate) with M_n up to 45000 reached in 6 hours.[30]

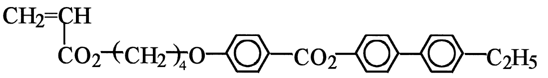
The success in polymerizing other monomers than styrene leaded the nitroxide polymerization to the preparation of copolymers comprising styrenic and nonstyrenic units, as, for instance, random copolymers of styrene and methyl methacrylate,[31] block copolymers based on styrene-butyl acrylate,[32] styrene-butyl methacrylate systems[33], styrene-acrylonitrile,[34] styrene-maleic anhydride[35] and styrene-choromethylstyrene.[36]

Preparation of special polymers by living/controlled radical polymerization

In spite of the great development of polymer science and of the increasing efforts in bringing out new living/controlled radical polymerization techniques, they have only been applied to the synthesis of the conventional polymers. The preparation of special polymers, e. g., liquid crystalline polymers, is a very interesting field of investigation for these methods, once such materials have many demanded properties which depend on their structure. Although being very opportune, the study of living radical techniques in the synthesis of LC polymers is still poor, few works being reported in this sense.

A first study done on the polymerization of special molecules by a living radical technique reported the synthesis of a PPV derivative using TEMPO as reversible terminator. The blue fluorescent product obtained with M_n = 37000 and MMD = 1.5 is suitable for light emission applications.[37]

Recently it was demonstrated that the living radical technique using TEMPO allows the accomplishment of the polymerization of liquid crystalline acrylates in a controlled way, when the LC monomer with structure **1** was polymerized, showing a behaviour of conversion that increased with time, M_n up to 6900 and MMD lowest as 1.47. The living character of the reaction was confirmed by chain extension with styrene into a block copolymer. In this pioneer work actual block copolymerization was achieved in 16 hours, yielding 34% of a product with M_n of 9700, starting from a macroinitiator with M_n = 6800. The effectiveness of the block formation was confirmed by ^{1}H-NMR and DSC analysis, that showed the transitions relative to the acrylate block and to the styrene one, clearly seen due to effective phase segregation reached, as showed in figure 1. [38]



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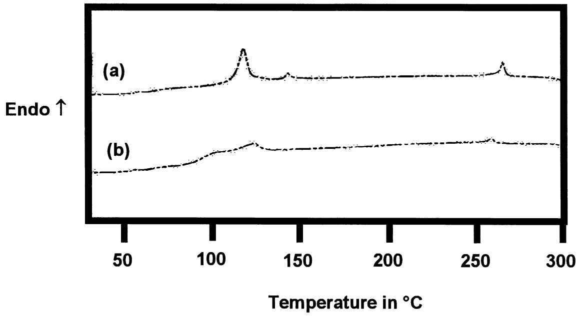


Figure 1. DSC curves for 3rd heating of (a) homopolymer and (b) copolymer sample.

Also the INIFERTER technique was applied to the synthesis of a LC block copolymer. Initially a telechelic polystyrene was thermally synthesized using N,N'-tetramethylthiuram-disulfide (TMTD) as INIFERTER, with a functionality value of ~1.8 obtained from the integration ratio of the ^{1}H-NMR signals and from GPC analysis. The block copolymer was obtained from UV radiation of the LC monomer in the presence of the telechelic polystyrene in THF. GPC analysis showed an increase in molecular weight of the block copolymer in relation to the polystyrene precursor, seen in Figure 2. Its composition, determined by ^{1}H-NMR spectrum, showed a molar ratio between styrene and LC segments of 1:9. [39]

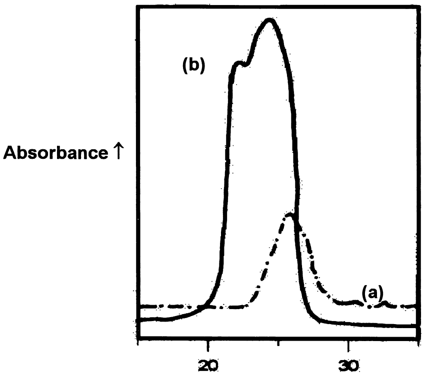
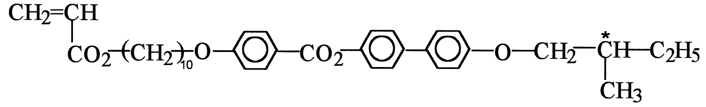


Figure 2. GPC curves of (a) thiuram terminated polystyrene and (b) block copolymer sample obtained therefrom.

To continue studying the application of living radical techniques to the synthesis of LC polymers, the systems based on SFRP and ATRP were investigated for the the polymerization of the LC monomer (**2**), structure-tailored to show ferroelectric properties.



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The polymerization of the LC monomer 2 trough SFRP was investigated in four variations which included two different initiators, the use of a TEMPO/AIBN adduct macroinitiator previously synthesized and of fructose as a reducing sugar. Table 1 summarizes the results for SFRP of the LC monomer 2 in all conditions tested.

Table 1: Results for the SFRP of the LC monomer 2

System	**Conversion (%)**	**M_n***	**MMD**
AIBN	76	2300	1.57
BPO	68	2300	1.51
TEMPO/AIBN adduct	60	2300	1.50
Fructose	80	2400	1.62

All reactions carried out in sealed glass ampoules; solvent: dioxane (1.0 ml); T = 135 °C; t = 48 hours.

* From GPC analysis.

The results found for the SFRP of the LC monomer seems to indicate a real limit to the chain growth, round $M_n = 2300$, even after changing the initiator and using artifices that should balance the nitroxide concentration in the reaction course.

After the polymerization of the LC monomer proven to be troublesome by TEMPO technique, was investigated the system based on ATRP, using an arenesulfonyl initiator (PDSC), catalyzed by CuBr and complexed by bpy. The system was thrice tested in the same conditions yielding results which were quite the same found for SFRP, as it can be seen in the Table 2.

Table 2: Experiences realized in ATRP for the LC monomer 2

Experience	**Conversion (%)**	**M_n***	**MMD**
I	65	2200	1.50
II	75	2300	1.52
III	70	2300	1.50

All reactions carried out in sealed glass ampoules; solvent: dioxane (1.0 ml); T = 130 °C; t = 48 hours.

* From GPC analysis.

Here, once more, the chain growth is stopped at a low value of M_n and the MMD is kept around 1.5. Just like in SFRP it seems to have a point where the chain growth is prevented. This possibly occurs due to the transfer reaction by the abstraction of the tertiary hydrogen of the chiral portion of the molecule, once these kind of results were totally different of those found for the polymerization of a monomer which differs from it only in this feature. [38]

Efforts taken to prepare styrenic copolymers starting from these macroinitiators by ATRP, according to the procedure described by Davis et al [40] were unsuccessfull and no copolymers were recovered after the reaction was stopped. An insight in these results is currently under investigation.

Thermal properties of the obtained homopolymer showed a mesophase between 53 °C to 93 °C, where relay the S_B and S_C transitions. The T_g transition, related to the acrylate chain is probably overlapped by the LC transitions. The short size of the mesophase is due to the low molar mass of the polymer. These results are in accordance with those once reported for ferroelectric polymers. [41]

Concluding remarks

In spite of the extensive number of studies investigated on living/controlled radical polymerization for ordinary monomers, its application to special polymers, such as liquid crystalline polymers, has been very rare. Once the LC monomers always bear complex structures and substituting groups its polymerization reaction is often different from the one related to conventional monomers, with very low reactivity and a great influence of hindrance and electronic effects.

Block copolymers with LC and amorphous moieties can be synthesized by living/controlled techniques by preparing a LC macroinitiator which is further chain extended with an amorphous monomer. The key for the overall process is the synthesis of the macroinitiator, because it is strongly influenced by the structure of the LC monomer, which always have structural characteristics that increase the rate of termination reactions. This behaviour is particularly observed in polymerizing a chiral monomer, where the tertiary hydrogen can suffer abstraction, dramatically preventing the chain growth, weather working on SFRP or ATRP.

Non-chiral LC monomers are suitably polymerized to higher molar masses than those found for the chiral one. Such monomers were successfully used in the preparation of block copolymers with styrenic segments by SFRP and INIFERTER technique, ensuring the usefullness of these methods in the preparation of such materials.

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