

Synthesis of block and graft copolymers containing liquid-crystalline segments

Ailton S Gomes,* Celton A Barbosa and Mauricio R Pinto

Instituto de Macromoléculas Professora Eloisa Mano (IMA), Universidad Federal do Rio de Janeiro (UFRJ), P O Box 68525, 21945-970, Rio de Janeiro, RJ, Brazil

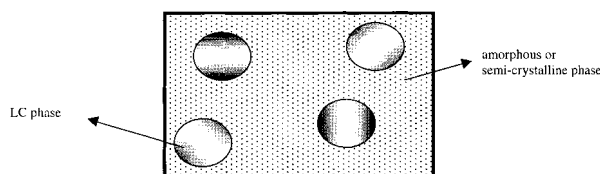
Abstract: Block and graft copolymers bearing amorphous or semi-crystalline and liquid-crystalline moieties were obtained by means of non-traditional synthetic routes. Chemical modification of block and graft copolymer precursors by molecular liquid crystals and controlled radical block copolymerization between liquid-crystalline monomers and styrene were used for this purpose. Controlled radical polymerization was accomplished by means of stable free radical polymerization (SRFP) and by INIFERTER methodologies. In the former methodology, 2,2,6,6-tetramethyl-piperidiny-1-oxyl (TEMPO) was used to mediate the propagation. The INIFERTER technique comprised the polymerization reaction between a liquid-crystalline monomer and a sample of thiuram-terminated polystyrene promoted by UV radiation. The performance of these techniques was evaluated taking into account the chemical composition of the materials produced. The thermal properties were determined by DSC and were correlated to the chemical composition of the polymers obtained.

© 1999 Society of Chemical Industry

Keywords: liquid crystal; block; graft; copolymers; polymer; chemical modification; thermotropic; macro-transfer; telechelic; INIFERTER; TEMPO; SRFP

INTRODUCTION

Block and graft copolymers are an interesting state of matter in respect of their morphologies, while the liquid-crystalline (LC) state contributes with unique thermal and flow properties. The combination of these different states of matter encompasses significant scientific and technological features. Liquid-crystalline polymers have a low compatibility with most conventional polymers, especially with those composed of hydrocarbon chains, such as polystyrene and polyolefins. Therefore, block and graft copolymers bearing amorphous or semi-crystalline and LC segments can give rise to microdomain segregation between the LC and non-LC moieties. A rough model of a macromolecular suprastructure originated from the phase-segregation process can be drawn. In Scheme 1 an example is shown, where the LC domains constitute the non-continuous phase. Desirable and eligible non-LC characteristics can be originated from the non-LC moieties without critical disturbance of the mesomorphic properties of the LC counterparts. For instance, mechanical strength and stiffness, film-forming and compatibilizing aid can be attained. In this way, a stiff and resilient film can physically support the LC state.



Scheme 1. Model of microdomain segregation between LC and amorphous or semi-crystalline phases of a block or graft copolymer.

Several relevant and recent methodologies of synthesis have been worked up: (i) polymer-analogous reaction of AB type prepolymers,^{1,2} (ii) ionic living block copolymerization between conventional and LC monomers and organometallic catalysed living insertion polymerization,^{3,4} and (iii) the use of macro-monomer and macroinitiator systems.^{5,6} Our synthetic goal to the synthesis of block and graft copolymers is based on the following:

- (1) Radical polymerization of an LC acrylate monomer in the presence of poly[ethylene-co-(vinyl acetate)] functionalized with thiol groups as macrotransfer agent.
- (2) Chemical modification of poly[styrene-co-tert-butyl acrylate], poly[styrene-co-(acrylic acid)] and

* Correspondence to: Ailton S Gomes, Instituto de Macromoléculas Professora Eloisa Mano (IMA), Universidad Federal do Rio de Janeiro (UFRJ), PO Box 68525, 21945-970, Rio de Janeiro, RJ, Brazil

Contract/grant sponsor: CAPES

Contract/grant sponsor: PADCT-FINEP

Contract/grant sponsor: CNPq

Contract/grant sponsor: CEPG/UFRJ

(Received 6 June 1998; accepted 11 February 1999)

the respective Li^+ , Na^+ , K^+ , Cs^+ and Bu_4N^+ ionomers by reactive low molecular weight liquid crystals.

- (3) Radical block copolymerization between styrene and an LC monomer by INIFERTER and TEMPO[®] techniques.

EXPERIMENTAL

Materials

2,2,6,6-Tetramethyl-piperidinyl-1-oxy (TEMPO), bis(*N,N*-dimethylcarbamyl)disulphide (thiuram disulphide), benzoyl peroxide (BPO), 4-phenylphenol, 4-chlorobutyl acetate, 1,4-dibromobutane, azoisobutyronitrile (AIBN), tetrabutylammonium hydroxide (solution 1M in methanol), tetrabutylammonium chloride, caesium hydroxide, trichloroacetic acid, dicyclohexylcarbodiimide (DCC), diethyl *N,N'*-azodicarboxylate, triphenylphosphine, titanium tetrabutoxide, diphenyl ether, *p*-toluenesulphonic acid and other non-specific reagents and solvents were purchased from commercial sources and used as received.

Toluenesulphonyl chloride was crystallized from hexane. Triethylamine, α -methylstyrene and ethyl ether were distilled over calcium hydride. Tetrahydrofuran and dioxane were treated with methylene diisocyanate (MDI) and then distilled over calcium hydride. Lithium, sodium and potassium alkoxides were obtained by dissolving the respective metals in methanol or in *tert*-butanol. Poly(lithium acrylate) was synthesized by neutralization of a commercial sample of poly(acrylic acid) with lithium methoxide.

Characterization

FTIR spectra were recorded on an IBM IR3x type 913X spectrometer equipped with Nicolet PC/IR operation software. Cast film obtained from evaporation of polymer solution over a KBr cell was used for this purpose. Spectra of the low molecular weight compounds were obtained from KBr pellets. ¹H and ¹³C-NMR spectra of CDCl₃ solutions were taken on a Varian DPX300 spectrometer. GPC and HPLC measurements were taken in a system composed of a Waters 600E pump, injector U6K, a Waters PDA 991 UV detector and a Waters 410 IR detector. For GPC measurements a series of three Ultrastayragel columns with porosity of 10⁵, 10⁴, 10³ and 10² Å and calibrated against polystyrene standards were used. THF solutions of the polymer samples were filtered through a Millipore membrane with a porosity of 0.45 μm just before injection. The UV-detection of the GPC analysis of the synthesized copolymers was set up for UV/vis quantitative analysis. A calibration curve was obtained from integration of the area under a standard peak. The standards used comprised model compounds of the respective LC segments used to synthesize the copolymer samples. Melting points of the molecular compounds and thermal properties of the polymer and LC materials were determined using a

Perkin Elmer DSC-7 series differential scanning calorimeter. Heating-cooling cycles were done at a rate of 20 °C min⁻¹, unless otherwise specified. Textures obtained by means of cross-polarized optical microscopy permitted the assignment of the respective LC phases in some cases.

Synthesis of LC monomers

4-Phenylazophenyl 4-[[4-[(1-oxo-2-propenyl)oxy]butyl]oxy]-benzoate (1)

The synthesis and characterization of this LC monomer is described elsewhere.¹⁰

4-Biphenyl 4-[[4-[(1-oxo-2-propenyl)oxy]butyl]oxy]-benzoate (2)

This monomer was synthesized in the same way as (1), but 4-phenylphenol was used instead of 4-phenylazophenol.⁷

4-(4'-Ethylbiphenyl) 4-[[4-[(1-oxo-2-propenyl)oxy]butyl]oxy]-benzoate (3)

The synthesis and characterization of this LC monomer is described elsewhere.⁸

4-[(4-Acetoxybutyl)oxy]biphenyl (4)

A mixture of 34.0 g (0.2 mol) of 4-phenylphenol, 56.1 g (0.25 mol) of 4-chlorobutyl acetate, 48.4 g (0.35 mol) of potassium carbonate and catalytic amounts of tetrabutylammonium chloride in 200 ml of *N,N*-dimethylformamide was heated at 100 °C with stirring for 12 h. The reaction was stopped by the addition of 600 ml of cold water. The waxy residue obtained was diluted with dichloromethane. The resulting solution was eluted through an aluminium oxide column with dichloromethane. The eluted solution was concentrated by evaporation, and a white solid was obtained after refrigeration of the concentrate. The product was filtered and dried under vacuum. Yield 54.4 g (76%); m.p. 79.1 °C; ¹H NMR (CDCl₃; ppm) δ = 1.93 (d, 2H), 2.22 (s, 3H), 4.05 (t, 2H), 4.20 (t, 2H), 6.97 (d, 2H), 7.32 (d, 1H), 7.41 (t, 2H), 7.55 (m, 4H); ¹³C NMR (CDCl₃; ppm) δ = 27.3, 64.5, 67.1, 115.0, 126.3, 128.4, 128.7, 128.9, 129.1, 133.2, 140.0, 158.0, 165.9; IR (KBr; cm⁻¹) 489, 688, 712, 1003, 1052, 1052, 1117, 1182, 1201, 1245, 1255, 1272, 1286, 1314, 1367, 1408, 1451, 1474, 1490, 1584, 1608, 1735, 2871, 2908, 2926, 2950, 3032, 3079.

4-[(4-Hydroxybutyl)oxy]biphenyl (5)

Hydrolysis of (4) was accomplished with an excess of potassium hydroxide in methanol under reflux for 2 h. The product obtained was crystallized twice from methanol. Yield 92%; m.p. 113.8 °C; ¹H NMR (CDCl₃; ppm) δ = 1.82 (m, 2H), 1.96 (m, 2H), 3.74 (t, 2H), 4.15 (t, 2H), 6.95 (d, 2H), 7.30 (d, 1H), 7.38 (t, 2H), 7.52 (m, 4H); IR (KBr; cm⁻¹) 492, 669, 690, 713, 1003, 1054, 1054, 1117, 1183, 1201, 1255, 1271, 1285, 1343, 1360, 1409, 1451, 1475, 1490, 1584, 1609, 2871, 2910, 2943, 3034, 3058, 3305.

4-[(4-Bromobutyl)oxy]biphenyl (6)

A suspension of 10.0 g (0.058 mol) of 4-phenylphenol, 38.0 g (0.174 mol) of 1,4-dibromobutane, 16.0 g (0.116 mol) of potassium carbonate and a catalytic amount of tetrabutylammonium chloride in 250 ml of butanone was refluxed with stirring for 48 h. The product was filtered and the solution obtained was diluted with a double amount of hexane. A waxy solid was obtained upon refrigeration of the resulting solution. The product was purified by column chromatography using basic aluminium oxide as stationary phase and dichloromethane as eluent. The solvent was evaporated and the remained white solid was crystallized from hexane/dichloromethane 1:1. Yield 12.5 g (70%); m.p. 82.2 °C; $^1\text{H NMR}$ (CDCl_3 ; ppm) δ = 2.05 (m, 2H), 2.12 (m, 2H), 3.58 (t, 2H), 4.09 (t, 2H), 7.00 (d, 2H), 7.34 (d, 1H), 7.45 (t, 2H), 7.58 (m, 4H); IR (KBr; cm^{-1}) 495, 595, 688, 716, 1007, 1045, 1120, 1180, 1203, 1244, 1257, 1277, 1280, 1317, 1408, 1449, 1462, 1490, 1584, 1608, 2874, 2929, 2944, 3007, 3034.

4-(4-Tosylbutyl)oxy]biphenyl (7)

10.0 g (4.13 mol) of (5) and 15.7 g (0.082 mol) of toluenesulfonyl chloride were dissolved in 250 ml of toluene. The resulting solution was cooled to 0–5 °C and then 11.5 ml (0.083 mol) of triethylamine was added dropwise under stirring. The reaction mixture was kept under a gentle flow of nitrogen and stirring for 6 h. The product was vacuum filtered and eluted through an acid aluminium oxide column with toluene. The eluted solution was concentrated by vacuum evaporation and a white precipitate was obtained after stepwise addition of cold hexane. The white solid obtained was dried and kept under vacuum. Yield 12.2 g (74%); m.p. 94.4 °C; $^1\text{H NMR}$ (CDCl_3 ; ppm) δ = 1.88 (m, 4H), 2.39 (s, 3H), 3.90 (t, 2H), 4.09 (t, 2H), 6.82 (d, 2H), 7.20–7.55 (m, 9H), 7.78 (d, 2H); $^{13}\text{C NMR}$ (CDCl_3 ; ppm) δ = 21.7, 25.5, 25.8, 66.4, 70.0, 114.2, 126.1, 127.2, 127.7, 128.3, 129.0, 132.5, 133.3, 140.0, 144.2, 157.7; IR (KBr; cm^{-1}) 498, 667, 715, 947, 1003, 1045, 1097, 1110, 1174, 1190, 1252, 1293, 1308, 1354, 1396, 1447, 1476, 1491, 1582, 1598, 2873, 2954, 2999, 3032.

Synthesis of polymer precursors**Thiol modified poly[ethylene-co-(vinyl alcohol)] (8)**

This macrotransfer agent was synthesized and purified as described elsewhere.¹⁰

Poly[styrene-block(tert-butyl acrylate)] (9)

This block copolymer was produced according to an adaptation of the procedure described by Tessie and co-workers.⁹ α -Methylstyrene was used instead of 1,1-diphenylethylene as blocking agent before the addition of the *tert*-butyl acrylate monomer. Molecular weight $M_n = 32\,049$, $M_w = 33\,420$, $M_w/M_n = 1.04$; $T_g = 35.2$, 92.0 °C; $^1\text{H NMR}$ (Py- d_5) δ = 1.41, 1.85, 2.03, 2.27, 6.59, 7.03 ppm; $^{13}\text{C NMR}$ (Py- d_5) δ = 28.7, 37.0, 41.3, 43.3, 126.5, 128.3, 128.9, 146.1, 174.5 ppm.

Poly[styrene-block-(acrylic acid)] (10)

20.0 g of (9), 1.0 g of *p*-toluenesulphonic acid in 150 ml of dioxane was refluxed for 24 h. The reaction mixture was added dropwise to a large quantity of ethyl ether. The precipitated polymer was precipitated again from dioxane solution by ethyl ether. The product was dried under high vacuum. Yield 12.0 g (80%); $T_g = 104.5$, 124.3 °C; $^1\text{H NMR}$ (Py- d_5) δ = 1.50, 1.71, 2.18, 2.40, 6.64, 7.08, 10.25 ppm.

Lithium (11a), sodium (11b), potassium (11c), caesium (11d) and tetrabutylammonium (11e) salts of poly[styrene-block-(acrylic acid)]

These ionomers were produced from treatment of poly[styrene-block-(acrylic acid)] (10) with an excess of alkaline metal alkoxides and with caesium and tetrabutylammonium hydroxide in dioxane. The resulting ionomers were precipitated by the addition of a large quantity of toluene. The precipitates were washed with methanol and dried under high vacuum.

Thiuram-terminated polystyrene (12)

A mixture of 30 ml of styrene and 1 g of bis(*N,N*-dimethylcarbonyl)disulphide was heated at 60 °C with stirring for 24 h in the absence of light. The polymer obtained was precipitated by addition of 300 ml of methanol and purified by another three steps of precipitation from tetrahydrofuran solution by methanol. The polymer was dried under high vacuum. Yield: 21.0 g; molecular weight $M_n = 2861$, $M_w = 5808$, $M_w/M_n = 2.03$; $T_g = 96.5$ °C.

Synthesis of copolymers**Reaction I. Graft reaction of the LC monomer (1) onto thiol modified poly[ethylene-co(vinyl alcohol)] matrix (8)**

This procedure is described elsewhere.¹⁰

Reaction II. Example of alkylation reaction of poly[styrene-block-(acrylic acid)] (10) by end-reactive liquid crystals

A mixture of 0.23 g (1.02 mmol of lithium acrylate units), 1.0 g (2.64 mmol) of (6) in 5 ml of HMPA was heated at 80 °C for 48 h with stirring. The reaction mixture was added to 200 ml of acetone. The precipitate formed was filtered and extracted with hot acetone. The polymer obtained was dissolved in a solution of 1 ml of trichloroacetic acid in 50 ml of dioxane and precipitated by the addition of 200 ml of ethyl ether. Yield 0.31 g.

Reaction III. Esterification reaction between poly[styrene-block-(acrylic acid)] (10) and 4-[(4-hydroxybutyl)oxy]biphenyl (5) promoted by DCC/Py condensation agent (III)

A mixture of 0.30 g (2.1 mmol of acrylic acid unit) of (10), 1.0 g (4.0 mmol) of (5), 0.82 g (4.0 mmol) of dicyclohexylcarbodiimide (DCC) and 2 ml of pyridine in 10 ml of dioxane was stirred at room temperature for 48 h. Dropping the mixture into 200 ml of methanol stopped the reaction. The polymer obtained was purified in the same way as described in reaction (II). Yield: 0.23 g.

Table 1. Reaction feed composition and yields of the graft copolymerization of the LC monomer onto EVAI-SH (8.8×10^{-3} wt%)

Run ^a	[SH]/[LCM] ^b $\times 10^{-3}$	Recovered LC monomer (wt%)	Recovered LC homopolymer (wt%)	Copolymer fraction (wt%)
1	39.1	49.0	5.6	45.4
2	19.5	57.6	3.8	38.3
3	7.8	65.3	4.9	29.8
4	3.9	56.1	15.0	28.9
Homopolymer	–	40.2	56.8	–

^a Polymerizations were carried out at 80 °C, in vacuo, for 48 h using 2 ml of toluene per gram of monomer and 1.5 mol% of AIBN with respect to the LC monomer quantity.

^b Molar ratio. Initial [SH] was obtained from iodometric analysis.

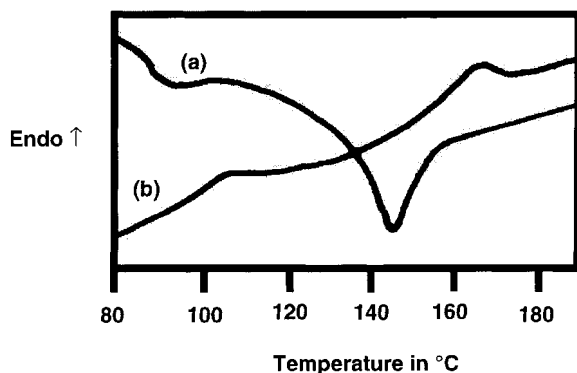


Figure 1. DSC curves of the poly[4-phenylazophenyl 4-[[4-[(1-oxo-2-propenyl)oxy]butyl]oxy]-benzoate] (9): (a) third heating and (b) third cooling scans.

(EVAI-SH; 8). The thiol groups are effective radical chain transfer agents, and become propagation sites in the polymer backbone.^{10,11} This macrotransfer agent was synthesized by the esterification reaction between 2-mercaptoacetic acid and a poly[ethylene-*co*-(vinyl alcohol)] sample (EVAI) shown in Scheme 2. Grafting was performed at LC monomer/EVA-SH mass ratios of 10, 5, 2 and 1 in the feed and using AIBN as radical initiator.

A homopolymer sample, poly[4-phenylazophenyl 4-[[4-[(1-oxo-2-propenyl)oxy]butyl]oxy]-benzoate], was prepared under the same conditions for comparison of reactivity and to provide information about spectroscopic and thermal transition assignments. All the graft copolymer samples synthesized had different solution properties in relation to the LC homopolymer and the precursor matrix. This difference allowed an efficient purification procedure, by which the graft copolymer could be easily separated from other polymeric impurities by selective solubilization and crystallization of crude product from hot toluene. The chemical composition of the graft copolymers was determined by means of elemental analysis and UV/vis spectrometry. The amount of LC segments in the copolymer samples ranged from about 5–30% (Table 1). These relatively low values can be explained by the fact that aromatic azo compounds can hinder radical polymerization somewhat. DSC curves of the homopolymer sample showed two enantiotropic transitions (Fig 1). Cross polarized light microscopy observations allowed the assignment of these transitions as

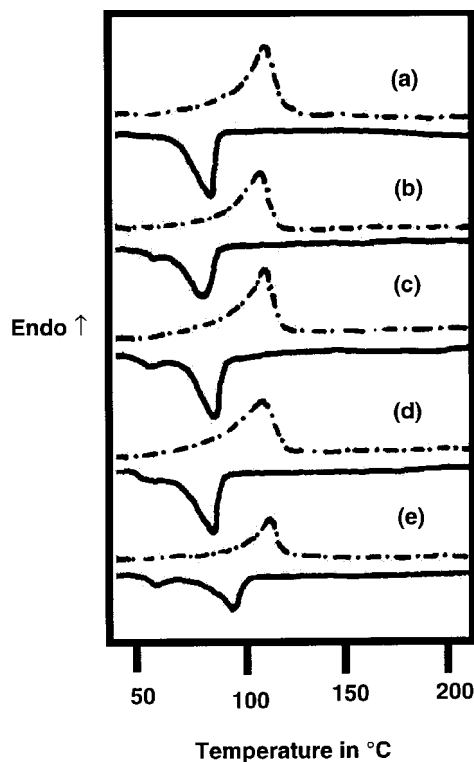
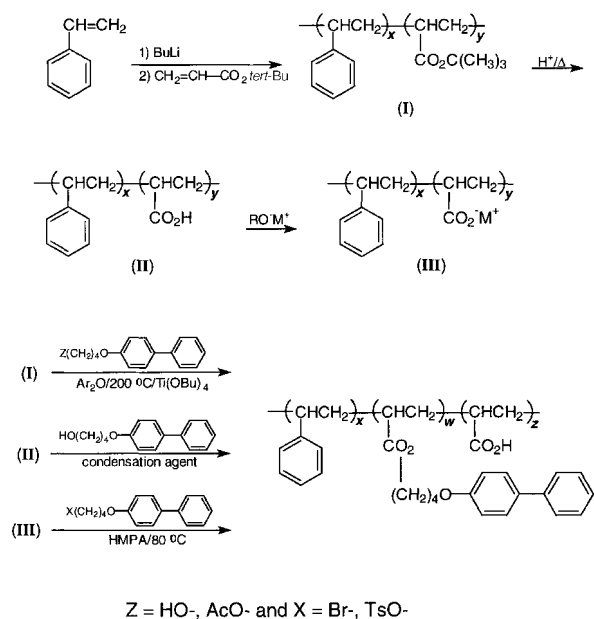


Figure 2. DSC curves of the copolymer samples: (a) EVA-SH; (b) copolymer 1; (c) 2; (d) 3 and (e) 4. For each sample the dashed line is the third heating scan and the solid one is the third cooling scan.

$K \leftrightarrow N \leftrightarrow 1$. The DSC curves of the graft copolymer samples showed a different pattern (Fig 2). Only the polyethylene melt peak could be observed during the heating scans. The crystallization peak of both LC and polyethylene domains could be observed during the cooling scans. The enthalpy of crystallization process of the polyethylene chains showed a straight-line relationship with chemical composition. Birefringence patterns of the graft copolymer samples were observed at 140 °C by microscopy techniques. No characteristic textures were observed due to low content of LC domains; probably they constitute non-continuous phase of segregated domains, which are not clearly seen by optical microscopy.

Chemical modification method

Block copolymers bearing styrene blocks and LC co-blocks were prepared by reaction between non-LC



Scheme 3

block copolymer precursors and low molecular weight liquid crystals with reactive end-groups (Scheme 3). Poly[styrene-*block*-(*tert*-butyl acrylate)] (**I**) was synthesized by a living anionic block copolymerization technique. GPC analysis confirmed actual block copolymerization. The polystyrene blocks showed the molecular weights $M_n = 17\,439$, $M_w = 18\,830$ and $M_w/M_n = 1.05$, while the block copolymer showed $M_n = 32\,049$, $M_w = 33\,420$ and $M_w/M_n = 1.04$. The chemical composition of this block copolymer was ascertained by NMR analysis, which indicated a styrene/*tert*-butyl acrylate molar ratio of 56:44. Quantitative hydrolysis of (**I**) under mild conditions produced poly[styrene-*block*-(acrylic acid)] (**II**). The feasibility of this reaction is enhanced by the good leaving properties of the *tert*-butyl groups under acid catalysis. Ionomers (**III**) of Li^+ , Na^+ , K^+ , Cs^+ and Bu_4N^+ cations were obtained from acid-base neutralization of (**II**) with the respective metal alkoxides and hydroxides.

The transesterification reactions between (**I**) and acetoxy- or hydroxy-terminated liquid crystals were catalysed by organotitanium under severe conditions or catalysed by *p*-toluenesulphonic acid under mild

conditions. The esterification reactions between (**II**) and a hydroxy-terminated liquid crystal were promoted by the condensation agents DCC/pyridine and $\text{Ar}_3\text{P}/\text{EtO}_2\text{C}-\text{N}=\text{N}-\text{CO}_2\text{Et}$ under mild conditions. A similar reaction was accomplished by organotitanium catalysis under severe reaction conditions. The ionomers (**III**) were alkylated by molecular liquid crystals bearing good leaving groups. The same reaction was accomplished using a sample of poly(lithium acrylate) for comparison of reactivity.

The amount of LC segments grafted onto the copolymer matrix was determined by UV quantitative analysis. The degrees of substitution of the esterification and transesterification reactions are grouped in Table 2. The reactions catalysed by acids did not give high values, though entry (1) is an exception. Most of the reactions conducted under severe conditions produced crosslinked gels. Intermolecular carboxylic anhydride bonds and titanium ionomer formation explain the gel formation. The carboxylic acid function brings about these side reactions, which compete with the grafting reaction. This explains the rapid gel formation in entry (6). The use of *tert*-butyl ester instead of carboxylic acid function, as the site of grafting reaction, rather precludes gel formation. Nevertheless, *tert*-butyl ester groups can be converted to carboxylic groups under the reaction conditions employed. Therefore, the gel formation in entry (2) is caused by conversion of the *tert*-butyl ester to the carboxylic acid function being faster than the grafting reaction. Entries (1) and (3) show opposite trends, and the difference between these entries can be attributed to the catalytic efficiency. Hence, organotitanium catalyst is more effective than protic acids in transesterification reactions. Entries (4) and (5) comprise the esterification reactions conducted under mild conditions. $\text{Ar}_3\text{P}/(\text{EtO}_2\text{CN}=\text{N})_2$ (known as the Mitsunobu reagent) is slightly less efficient than the traditional DCC/pyridine condensation agent. The former system is highly reactive, because the reaction took place in just a few minutes (observed from cessation of gas evolution and reaction colour change). Consequently, the reaction was controlled by diffusion of the reactants. Both reactions showed an increase in molecular weight in relation to the expected value because of intermolecular carboxylic anhydride bond formation.

Table 2. Degree of substitution obtained from UV quantitative analysis of block copolymers obtained via transesterification and esterification reactions

Entry	Reactive groups	Polymer/molecular LC	Method	Degree of substitution ^a
Transesterification				
1	$-\text{CO}_2\text{tert-Bu}-\text{OH}$		$\text{Ti}(\text{nBuO})_4/200^\circ\text{C}$	28.6
2	$-\text{CO}_2\text{tert-Bu}-\text{OAc}$		$\text{Ti}(\text{nBuO})_4/200^\circ\text{C}$	Crosslinked
3	$-\text{CO}_2\text{tert-Bu}-\text{OH}$		$\text{TsOH}/100^\circ\text{C}$	7.8
Esterification				
4	$-\text{CO}_2\text{H}-\text{OH}$		DCC/Py	25.2
5	$-\text{CO}_2\text{H}-\text{OH}$		$\text{Ar}_3\text{P}/(\text{EtO}_2\text{CN}=\text{N})_2$	16.0
6	$-\text{CO}_2\text{H}-\text{OH}$		$\text{Ti}(\text{nBuO})_4/200^\circ\text{C}$	Crosslinked

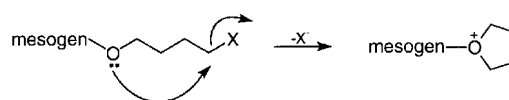
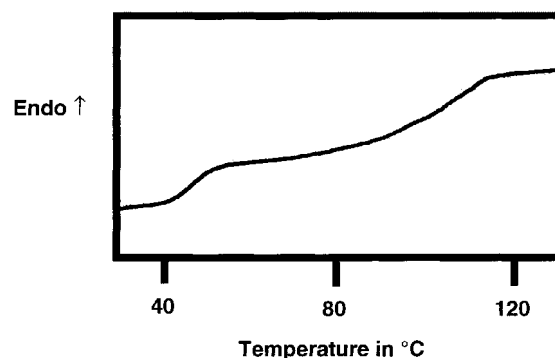
^a Molar ratio between initial acrylic acid *mer* content and final acrylic ester content.

Table 3. Degree of substitution obtained from UV quantitative analysis of block copolymers obtained via alkylation of ionomers

Counterion	Displaced group	Degree of substitution ^a
Poly(Li ⁺ acrylate)	Br ⁻	33.7
Li ⁺	Br ⁻	24.4
Li ⁺	TsO ⁻	30.2
Na ⁺	Br ⁻	15.6
K ⁺	TsO ⁻	2.8
Cs ⁺	Br ⁻	5.6
Cs ⁺	TsO ⁻	4.6
<i>n</i> -Bu ₄ N ⁺	Br ⁻	17.9

^a Molar ratio between initial acrylic acid *mer* content and final acrylic ester content in the block copolymer sample.

The results pertaining to the degree of substitution of the alkylation reactions of ionomers by reactive molecular LCs are grouped in Table 3. Regardless of the Bu₄N⁺ ionomer, all runs were initially heterogeneous; however, they became homogeneous as the alkylation reaction proceeded. The best results were obtained from lithium ionomer, while the tetrabutylammonium ionomer showed an intermediate performance. The homopolymer poly(lithium acrylate) showed a higher reactivity than the corresponding block copolymer. This observation implies that the polystyrene blocks are responsible for the reduced reactivity, and somehow frustrate the reaction between the acrylate segments and the reactive low molecular weight compounds. Another possibility that explains this difference in reactivity is related to the differences in configuration of the acrylate backbone, because both samples were prepared from different reaction mechanisms. Differences in polymer chain tacticity may contribute to differences in nucleophilic strengths of the carboxylate anions linked to the respective polymer chain. The difference of reactivity observed among the ionomers is related to the effects of the degree of solvation of the cations and the electrostatic interaction between the carboxylate anion and its counterion. Lithium ions are best solvated by HMPA, which improves the nucleophilic power of the carboxylate anion. The opposite effect is observed from caesium ionomer. Counterions solvated to a lesser extent lead to the formation of ion pairs, ie there are still electrostatic interactions between anions and cations, which decrease the nucleophilic power of the anions. Tetrabutylammonium is a bulk organic cation, and it can be solvated by organic solvents, but still remains somewhat interacted with the carboxylate anions. No trends of reactivity can be observed between the molecular liquid crystals bearing tosyl and bromine leaving-groups. Perhaps the effects of the counterions are much more expressive than a slight difference of reactivity between the tosyl and bromine leaving-groups. The lack of difference of reactivity between these groups may be attributed to anchimeric assistance of the oxygen atom to the departure of the leaving-group (see Fig 3). A new reactive intermediate is the actual alkylating agent, and its formation occurs

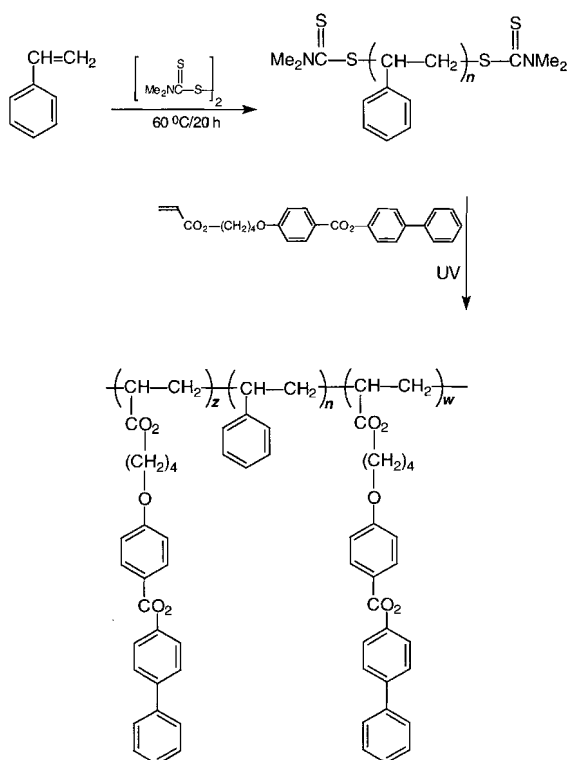
**Figure 3.** Anchimeric assistance mechanism. A new reactive intermediate may take part in the ionomer alkylation reactions.**Figure 4.** Third DSC heating curve of the poly[styrene-*block*-(lithium acrylate)] alkylated by 4-[(4-bromobutyl)oxy]biphenyl.

at nearly the same ratio regardless of the type of leaving-group.

DSC curves of the modified polymers showed only two glass transitions. That near 105 °C corresponds to the polystyrene segments, while the other, which oscillates with the degree of substitution between 40 and 60 °C corresponds to the acrylic segments as depicted in Fig 4. The absence of mesomorphic phases can be explained by the fact that the biphenyl units have a low axial ratio. Consequently, these mesogenic units have a low probability to develop mesomorphic order. In fact, the respective homopolymer sample did not show LC properties. This homopolymer sample was synthesized from radical polymerization of an LC monomer bearing biphenyl units. Nevertheless, the information obtained from the reactions between block copolymer precursors and biphenyl-based molecular compounds serves as a basis of reactivity comparisons for other systems.

Block copolymerization between styrene and 4-biphenyl 4-[[4-[(1-oxo-2-propenyl)oxy]butyl]oxy]benzoate was accomplished by means of the INIFERTER technique (Scheme 4). Thiuram terminated polystyrene was synthesized by thermal polymerization promoted by *N,N'*-tetramethylthiuram-disulphide (TMTD). A functionality value of about 1.8 was obtained from the integration ratio of the ¹H NMR signals at 3.1–3.6 ppm (CH₃—N protons present in the end-groups) and at 6.2–6.8 ppm (aromatic ring protons) in conjunction with the molecular weight values obtained 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 (Fig 5). The peak of the copolymer sample was bimodal. GPC



Scheme 4

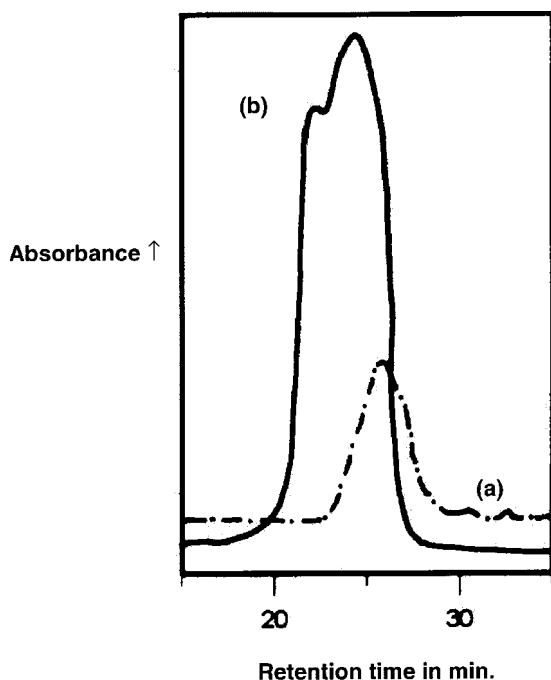


Figure 5. GPC curves of (a) thiuram-terminated polystyrene and (b) the block copolymer sample obtained therefrom.

fractionating gave an LC homopolymer and a block copolymer fraction in a proportion of 1:5. The block copolymer fraction ¹³C NMR spectrum showed the presence of a peak at 42 ppm, which was assigned to the CH₃-N present in the thiuram end-groups. The composition was determined from the ¹H NMR spectrum, which showed a molar ratio between polystyrene and LC segments of 1:9. This value was

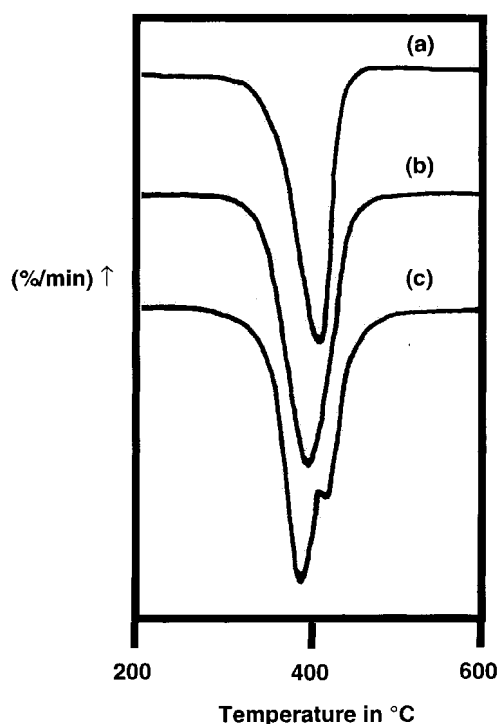


Figure 6. DTGA curves (20 °C min⁻¹) of (a) thiuram-terminated polystyrene, (b) LC homopolymer, and (c) block copolymer samples.

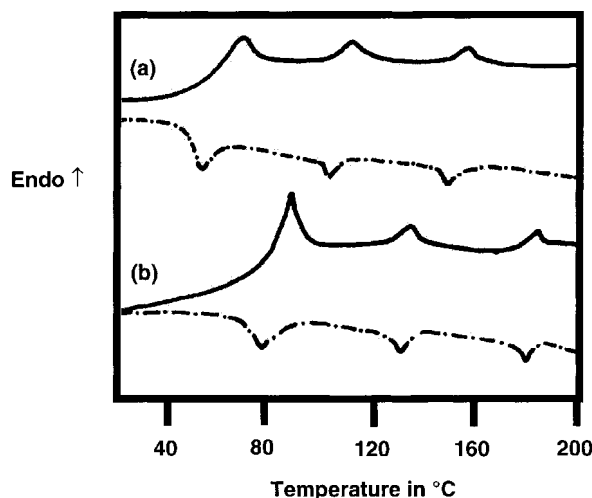
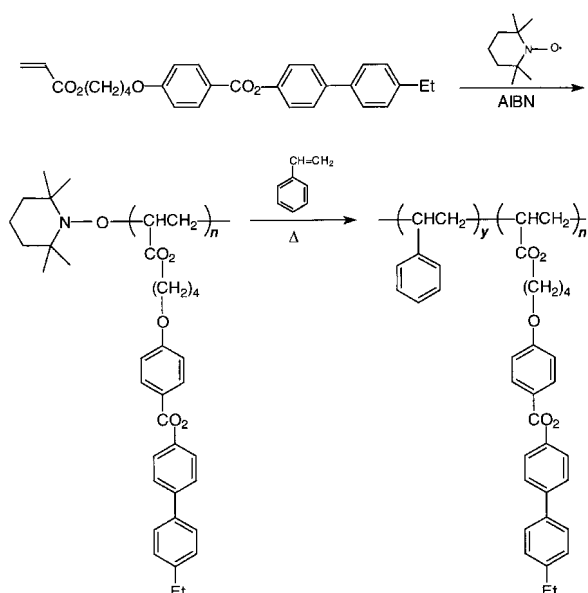


Figure 7. DSC curves of (a) LC homopolymer and (b) block copolymer. Solid lines are related to the third heating scan and dotted lines to the third cooling scan.

expected because the mass ratio of polystyrene and LC monomer in the reaction feed was 1:10, and some polystyrene precursor was recovered at the end of polymerization reaction. Thermal analyses of the polystyrene precursor, LC homopolymer and block copolymer samples were carried out by the DTGA and DSC techniques. DTGA curves indicated actual block copolymerization (Fig 6). The DSC curves of the LC homopolymer and block copolymer sample were similar. Three enantiotropic transitions were assigned in conjunction with cross-polarized light microscopy observations, as $g \leftrightarrow S \leftrightarrow N \leftrightarrow I$ transitions (Fig 7). The



Scheme 5

slight difference between the homo and copolymer curves was attributed to differences in molecular weight of the LC segments. The T_g of the polystyrene segments was overlapped by the K→S liquid crystalline transition.

Block copolymers bearing polystyrene and LC components were also obtained by the stable free radical polymerization (SFRP) technique. 2,2,6,6-Tetramethylpiperidiny-1-oxy (TEMPO) was used in the homo and block copolymerization reactions. This stable free radical traps the radical of the chain propagation initiated by AIBN. An equilibrium between the new polymer-TEMPO end bond and a free radical is established under the reaction conditions, and this controls the propagation steps. Hence, the molecular weight and dispersion can be controlled mainly by the relative amounts of monomer, initiator and TEMPO. The homopolymers produced retain the TEMPO termination even after purification procedures. Thus, block copolymerization can be accomplished afterwards. The synthetic route is outlined in Scheme 5. Different homopolymer samples were obtained from variation of the initiator/TEMPO concentration ratio. The data obtained from these polymerizations are grouped in Table 4.

The variation of the ratio between [I] and [TEMPO] was investigated because of the controver-

Table 4. Characteristics of LC polymers obtained by SFRP

Homopolymer	[I]/[TEMPO] ^a	Conversion (%)	M_n ($g\ mol^{-1}$)	PDI
1	1.2	78	6800	1.49
2	1.0	76	6900	1.47
3	0.83	76	6900	1.47

^a is the initiator AIBN; polymerizations were run in dioxane at 135 °C for 48 h in sealed ampoules.

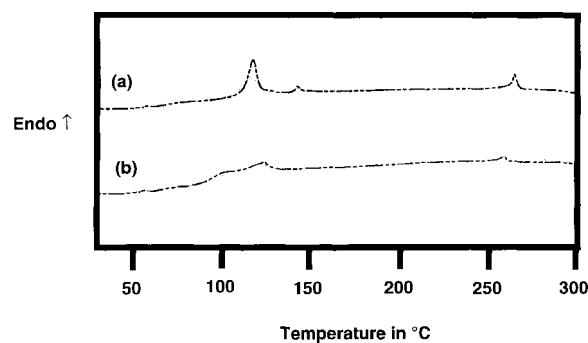


Figure 8. DSC curves for the third heating of (a) homopolymer and (b) copolymer sample.

sial results that have been reported about this technique. Some works state that improved efficiency requires excess of initiator,¹² while others claim that the nitroxide must be in excess for better results.¹³ The results obtained from the LC monomer homopolymerization indicate that both situations and equimolar amounts of initiator and nitroxide can be successfully used if the ratio between them is near unity.

The GPC results of polymer (2) show very interesting behaviour for the free radical polymerization of a LC monomer. The values of molecular weight dispersion (PDI) observed are lower than the predicted values inherent to conventional free radical polymerizations, such as 1.5, and indicate a controlled reaction.

The ¹H NMR spectra showed multiple peaks at $\delta = 1.0$ ppm, which were assigned to the methyl protons of the piperidine fragment. These peaks verify the homopolymer samples have nitroxide end-groups.

Another homopolymer sample was probably synthesized with molecular weight of 6800 and PDI of 1.67. This sample was further block copolymerized with styrene under the same conditions for 16 h. A monomodal copolymer with M_n of 9700 and PDI of 2.61 was obtained, and a 34% yield was achieved. Hence, the second monomer was exclusively converted to the block copolymer, which is an indication of the living fashion of the polymerization reaction.

The DSC curves of the homopolymer samples showed a second order transition at 73 °C. This high T_g change relative to acrylate chains is attributed to the rigidity of the side-chains (Fig 8, curve a). Liquid crystalline states could be observed between 115 and 263 °C during the heating scans, and T_g -K-S-N-I phase transitions could be assigned. The copolymer DSC curves showed two T_g transitions (Fig 8, curve b). The first appeared in the same position in relation to the homopolymer curve, and is related to the thermal motions of the acrylate blocks. The second, located at around 100 °C is characteristic of the T_g of the polystyrene blocks. An evidence of effective phase segregation between polyacrylate and polystyrene moieties comes from the observation of these two clear-cut separated T_g transitions. The heating curve also showed the same LC phase transitions in relation

to the homopolymer one, but in a less defined pattern. The size dispersion of the polystyrene blocks and of the LC microdomains spread within the continuous polystyrene phase, the interface interaction between the segregated phases and other minor effects are responsible for the observed depletion of the structured shape of the LC phases transitions.

CONCLUSIONS

Graft and block copolymers bearing amorphous or semi-crystalline and liquid-crystalline segregated domains could be obtained from innovative methodologies. The chemical modification method allows good structural control. The disadvantage of this method still remaining is the poor chemical composition control, albeit it can offer a wide choice of substrates. Previously synthesized macrotransfer or macro-initiator reactants accomplished block and graft copolymerization via radical polymerization of LC monomers. Apart from the SFRP method, these polymerizations allowed less structural control, because polydisperse liquid crystalline segments were produced. The advantage of this method relies on the better chemical composition of the copolymers. The SFRP method provides controlled polymerization; moreover monodispersed LC polymers could be obtained. The disadvantage of the radical polymerization based methods is related to the homopolymer and polymer precursor contaminants. This can be overcome by appropriate choice of the chemical structures, which differentiate the polymer contaminants from the copolymer sample by means of any physical or

chemical property. When copolymer and polymer contaminants have different solution properties, efficient separation of the constituents of a product mixture can be accomplished by simplified precipitation techniques.

ACKNOWLEDGEMENTS

The authors wish to thank CAPES, PADCT-FINEP, CNPq and CEPG/UFRJ for financial support.

REFERENCES AND NOTES

- 1 Adams J, Sanger J, Tefehne C and Gronski W, *Macromol Rapid Commun* **15**:879 (1994).
- 2 Arnold M, Poser S, Fischer H and Utschick W, *Macromol Rapid Commun* **15**:487 (1994).
- 3 Bohnert R and Finkelmann H, *Macromol Chem Phys* **195**:689 (1994).
- 4 Yamada M, Iguchi T, Hirao A, Nakahama S and Watanabe J, *Macromolecules* **28**:50 (1995).
- 5 Pugh C and Percec V, *Am Chem Soc Polym Prepr* **27**:366 (1986).
- 6 Chiellini E and Galli G, *Macromol Symp* **77**:349 (1994).
- 7 Detailed characterization will be described in a future publication.
- 8 Barbosa CA and Gomes AS, *Polym Bull* **41**:15 (1998).
- 9 Fayt R, Forte R, Jacobs C, Jerone R, Ouhadi T and Teyssie Ph, *Macromolecules*, **20**:1442 (1987).
- 10 Pinto MR, Gomes AS and Soares BG, *Macromol Chem Phys* **197**:2103 (1996).
- 11 Gomes AS, Carvalho KS and Pinto MR, *Macromol Rapid Commun* **16**:543 (1995).
- 12 Grezsta D, Mardare M and Matyjazewski K, *Macromolecules* **27**:638 (1994).
- 13 Veregin RPN, Odell PG, Michalak LM and Georges MK, *Macromolecules* **29**:2746 (1996).