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Liquid-crystalline polyacrylate crosslinked with α, ω polyisoprene diacrylate segments

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Summary

The preparation of functionalized *cis*-1,4-polyisoprene and its copolymerization with a liquid crystalline monomer are reported in this paper. A sample of natural rubber *Hevea Brasiliensis* with HO end group was reacted with acryloyl chloride. The copolymerization between telechelic acrylate polyisoprene and [(4’-methylphenyl)benzoyloxy-4-oxytetramethylene] acrylate (LCM) was performed by radicalar reaction using 2,2’- azoisobutyronytrile as the initiator. The LCM incorporation into the copolymer was analysed by ^{1}H NMR and TGA measurements. The product exhibits liquid crystalline properties observed by polarized optical microscopy and DSC. Some particular mechanical properties were also evaluated by oscillatory tests.

Introduction

Crosslinked liquid crystal elastomers represent important model substances in order to understand the influence of its structure on liquid-crystalline behavior(1-3). Most of these materials contain the mesogenic group as a side chain moiety due to the favorable molecular architecture for the obtenation of liquid-crystalline properties in polymeric systems. This class of elastomers is of interest with respect to scientific research and technological applications(4). Although moderate levels of chemical crosslinking have been used to enhance rubberlike properties and to increase resilience of the material, crosslinks can modify the interaction between the mesogenic units and the polymer backbone (4,5). Therefore, valuable information about the interaction between main chain conformation and liquid-crystalline order of the mesogenic side chain group are obtained by mechanical deformation of the network(6).

Most of the synthetic routes are based on polymerization of acrylated liquid-crystalline monomer(2,5,7) and on incorporation of nematogenic moieties onto polysiloxanes(8,9). Usually, a few amounts of bifunctional comonomer is added in order to attach functionalized groups to the main chain for later crosslinking reactions.

In a previous publication we have reported the preparation of block copolymers containing poly(propylene oxide) segments and liquid-crystalline polyacrylate(10). In this communication, we describe the synthesis of a crosslinked copolymer prepared from

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telechelic α,ω-diacrylate functionalized polyisoprene and [(4'-methylphenyl)benzoyloxy-4-oxytetramethylene] acrylate by radicalar reaction.

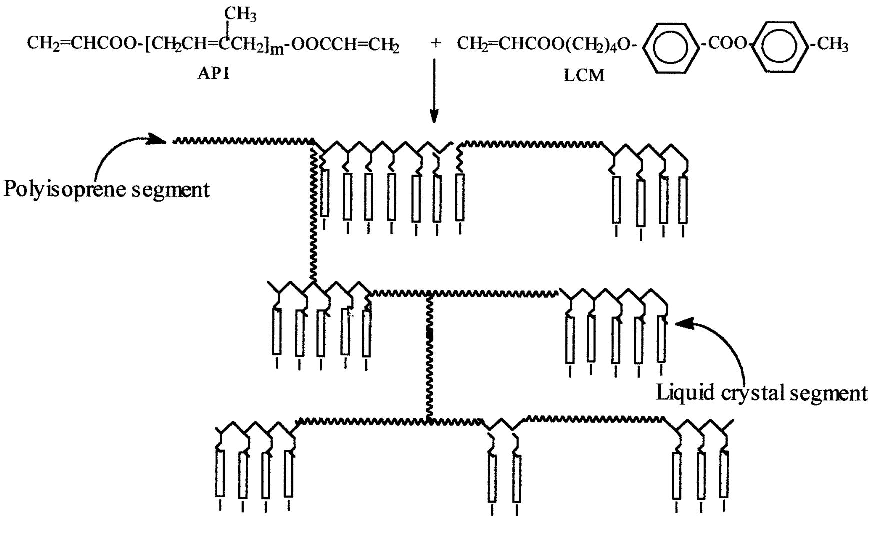
Experimental Part

Synthesis of telechelic α,ω acrylate functionalized polyisoprene

All the steps involved in the synthesis of telechelic OH-polyisoprene were performed according to our previous work(11,12). The reaction of OH-telechelic polyisoprene with acryloyl chloride was carried out in dry THF under stirring at room temperature. At first, acryloyl chloride and dry triethylamine were added by syringe into the OH-telechelic polyisoprene solution at -42°C in a small stechiometric excess. The system was slowly heated to room temperature and left to react for 42 hours under argon atmosphere. The reaction was ended by adding slowly a small amount of water. Afterwards, the reaction mixture was washed with a saturated NaCl solution and distilled water. The solvent was evaporated and the polymer was dried under vacuum at room temperature.

Synthesis of the block copolymer

Telechelic α,ω acrylate functionalized polyisoprene (API) and [(4'-methylphenyl)benzoyloxy-4-oxytetramethylene] acrylate, liquid-crystalline monomer (LCM), were mixed in the desired ratio with a small amount of AIBN (~2%) and dissolved in toluene. The solvent was previously purified and bubbled with nitrogen for at least 2 hours. The Petri dish, which contents the solution, was placed in a flat bottom chamber. The reaction was performed for 72 hours at 70°C ~ 80°C under constant flux of nitrogen through the chamber. The thin film of formed copolymer underwent extraction with acetone in a Soxhlet apparatus for 4 hours to remove any trace of LCM homopolymer. Finally, the product was dried under vacuum. The predicted structure of the copolymer is depicted below.



Copolymer characterization

The ^{1}H-NMR spectra of the materials, including the crosslinked copolymer, in the swollen state, were recorded in a Varian XL-200 spectrometer at 20 °C using a sample solution in $CDCl_3$ with TMS as reference. The thermal properties of the materials were determined by a DuPont 2100 calorimeter, measuring after the second heating-cooling cycle at a rate of 10 °c/min from -80 °C to 230 °C. Optical polarizing microscopy analysis were performed in a Leitz-Leica Laborlux 12 POL S microscopy using a LINKAM THMS 600 heating/cooling apparatus. Thermal gravimetric analysis were performed on a Dupont TGA 2950 at a rate of 10 °C/min.

Vibratory tests were carried out in the stress controlled rheometer Rheometrics SR-200. Samples were put between 25 mm parallel plates. Small sample discs with 1 mm to 2 mm thickness were tested, fitting their diameters and the applied stress to the torque limitation of the instrument and to ensure an analysis in the linear viscoelastic region, respectively. The results were meaningful for qualitative estimates.

Results and discussion

As reported previously(10, 11), the polyisoprene with HO end groups was obtained from the oxidative degradation of *Hevea Brasilienses* rubber (>98% cis) followed by reduction with $LiAAlH_4$. The HO end groups were reacted with acryloyl chloride to obtain the polyisoprene with acrylated (API) end groups. The radical copolymerization of API and LCM formed films with few bubbles and reasonable elasticity.

The incorporation of LCM on the copolymer was characterized by ^{1}H-NMR despite difficulties in preparing the samples due to the crosslinking (Figure 1) and by TGA measurements (Figure 2).

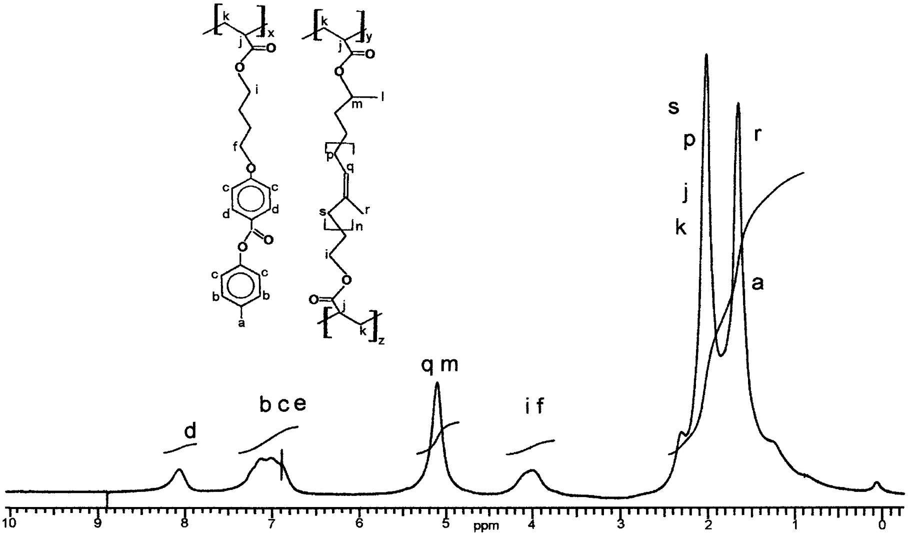


Figure 1 – ^{1}H NMR of the API/LCM block copolymer with 44.5% of LCM

The LCM content was determined by ^{1}H NMR comparing the integral of the signal at $\delta \approx$ 4ppm due to 4H (-OCH-) of LCM and 2 H (-OCH-) of polyisoprene with the one at δ ≈ 5.2 ppm attributed to the =CH polyisoprene signals which correspond to the polysisoprene *mer*.

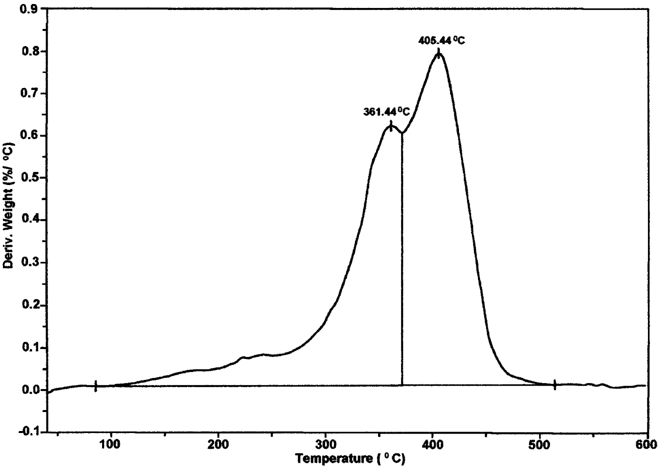


Figure 2 – TGA thermogram of the copolymer prepared with 30.3% of LCM

TGA thermograms, (Figure 2) present the decomposition behavior of the copolymer. The polyisoprene with OH end groups possesses a maximum in the degradation rate at 367 °C and the LCM homopolymer exibits two maxima at 386 °C, suggesting a depolymerization reaction of acrylated segments, and at 406 °C due to decomposition. For the measurement of the LCM contents the area of the peak at ~ 405°C was used.

Table 1 shows the incorporation of LCM increasing with the amount of LCM in the reaction mixture. The amount of LCM in the copolymer is apparently higher than in the feed. The extraction following the copolymerization with acetone did not remove only unreacted LCM, LCM homopolymer, but also polyisoprene oligomers. We acchieved a good agreement between the two techniques even for the experiment 6 in which the incorporation of LCM was lower than expected.

Table 1 - Incorporation of liquid crystal in the copolymer

Experiment	Polyisoprene Mn	LCM in the feed w%	LCM in the copolymer NMR (w%)	LCM in the copolymer TGA (w%)
1	2600	15.9	20.8	25,4
2	2600	17.5	21.9	-
3	2600	24.2	25.9	28.2
4	2600	28.4	40.4	41.0
5	2600	30.3	55.9	54.8
6	2600	44.5	34.0	31.9
7	2100	46.5	58.7	-
8	2100	50.0	-	61.1

*Mw/Mn ≅ 4.0

The crosslinked copolymer samples were opaque and when observed by microscopy, birefrigent up to ~ 90°C. In cooling step from the isotropic state, the birefringence has been observed when it was cooled down ~ 90°C. LCM has a melting point at 61.8 °C and it requires some degree of polymerization to raise mesomorphic state as shown in figure 3. The DSC second heating curves of the copolymers show the isotropization transition extended over a broad range of temperature between ~90 °C and ~230 °C. This broadening was associated with the different lengths of LCM segments once it has been demonstrated the influence of the degree of polymerization in the range of mesophase (13). The Tg of the LCM segment changes from 16 °C in the homopolymer to about 30 °C in the copolymer. Melting transitions in the homopolymer were displaced from about 53 °C to 36-38 °C in the copolymers and the one with high LCM contents still presents a small endothermic peak around 53 °C indicating long LCM segments. The Tg of polyisoprene was also affected by the LCM incorporation. Eventually, the thermal behavior of the copolymers seems to have tight correlation to the characteristic flexibility of the elastomeric part and crosslinking density.

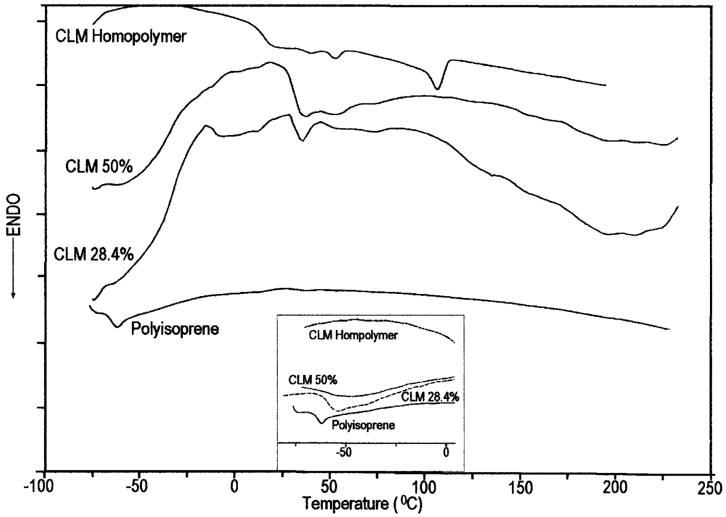


Figure 3- DSC curves obtained from the LCM homopolymer and copolymers containing 50% and 28.4% of LCM

Dynamic mechanical responses taken from complex viscosity curves (η^*), depicted in Figure 4(a), show a discontinuity in the frequency range from 4 x 10^0 Hz to 2 x 10^1 Hz, where the viscosity decreases curtly to reach a lower level. This phenomenon, which was not observed in an API sample (Figure 4(b)), became sharper in copolymers as temperature was raised. This can correlate to a biphasic behavior of the copolymers.

Stress relaxation of polyisoprene and liquid-crystalline blocks occurs more homogeneously at lower temperatures due to low mobility of chain segments. The one with higher reptation time could have a function of anchorage to the other, leading to uniform stress relaxation of the system. The heating enlarges the free volume of the system and facilitates segregation of the incompatible phases. Incompatibility between phases is a reasonable explanation for the appearance of discontinuities in the η^* curves due to strong differences in polarity and structure between components of the copolymer. Furthermore, the displacement of this discontinuity to higher frequency at higher temperatures owes to shortening of the relaxation time of both phases. Besides, more viscous component could be prompted to get premature relaxation induced by high mobility of the less viscous phase.

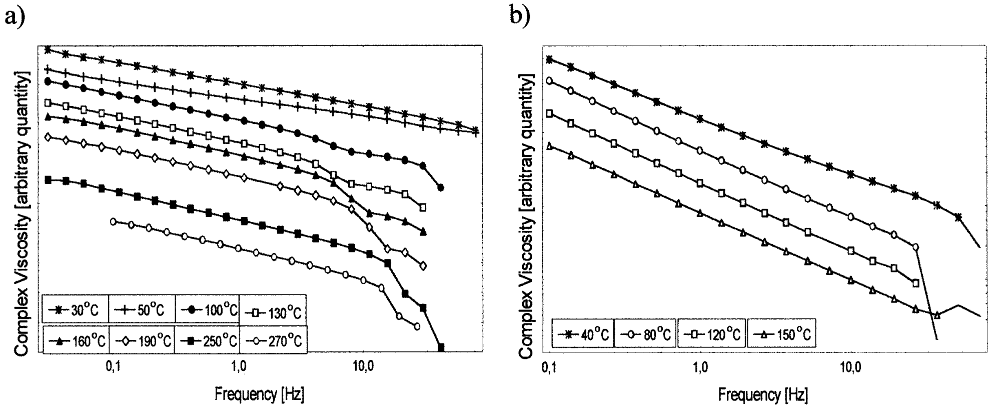


Figure 4: Complex viscosity data at several temperatures taken from (a) a copolymer prepared with 39,2 wt% of LCM and (b) API; frequency sweep test.

Mesomorphic order can be correlated the ratio $|d\eta^*/d\omega|$. At low frequencies, before the discontinuity point, $|d\eta^*/d\omega|$ is larger for curves taken at temperatures above 100°C (isoptropic state). The following sequence for $|d\eta^*/d\omega|$ has been obtained:

$270°C \cong 250°C \cong 190°C \cong 160°C \cong 130°C \cong 100°C > 30°C > 50°C$

There is a great possibility to find ordered structures below 100°C even under the oscillatory conditions imposed by frequency sweep analysis. This order decreases the entropy of the system as well as the mobility of some chain segments. The stiffness of the material partially originated at anchorage effects will be maintained. This results in a small change of η^* with frequency in non-isotropized samples when compared to a biphasic state. Lower values of $|d\eta^*/d\omega|$ at 30°C and 50°C can be attributed to melting liquid-crystalline blocks, observed in DSC thermograms at 36°C-38°C. At 50°C mesogenic group ordering is thermodynamically favored, enhancing the trend discussed above. However, this tendency becomes weaker as the entropy level is increased by raising temperature until it is overcome by phase segregation trends.

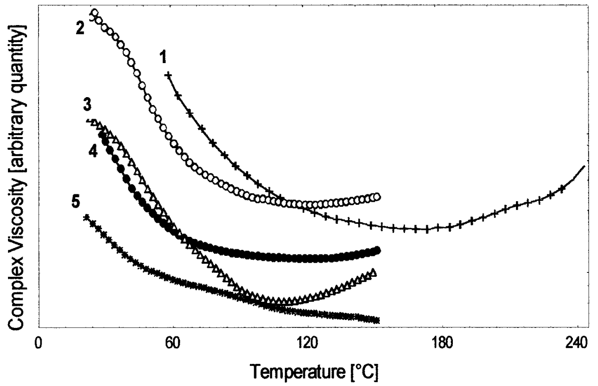


Figure 5: Complex viscosity obtained by temperature sweep test at frequency of 1 Hz from homopolymerized α,ω-polyisoprene diacrylate (5) and copolymers prepared with 50 wt% (1), 30,3 wt% (2), 28,4 wt% (4) and 9,5 wt% (3) of LCM.

Temperature sweep analysis, shown in Figure 5, reveal the influence of liquid-crystalline blocks on rheological parameters of polyisoprene. At temperatures below the isotropization point, the viscosity drop ratio with temperature, $d\eta^*/dT$, is larger in copolymers than in homopolymerized acrylate telechelic polyisoprene. Under these conditions, mesogenic groups can enhance viscosity drops due their ordered character. As a matter of fact, the system probably reaches partial order within the short cycle time (1 second). The organization of some moieties along the stress direction provides lower resistance to deformation of the material and causes strong decreases in viscosity. Zentel et al (14) reported that deformations as small as 20% are enough to generate mesomorphic order in achiral elastomeric liquid crystals. Deformations up to 26% were found in these tests.

At temperatures above 100°C, $d\eta^*/dT$ become positive in copolymers, while homopolymerized polyisoprene keep the negative slope over the total range of temperature. De Abajo et al (15) reported a similar behavior in main chain liquid-crystalline polymers. The phenomena were explained by disordering effects of mesogenic groups in the isotropization process, which increases the flow resistance. Investigating negative $d\eta^*/dT$ into positive ratiosis more pronounced in copolymers with larger amounts of LCM. The storage modulus behaves in the same way as the complex viscosity, in accordance to the data obtained by Datta and Baird (16).

Conclusion

Characteristic liquid-crystalline behaviors are inherited when natural rubber is copolymerized with a liquid-crystalline precursor. Thermal properties of the copolymers are strongly affected by the crosslinking density and demand a detailed investigation for a comprehensive undestanding of kinetic and thermodynamic phenomena. Dynamic mechanical analyses have revealed biphasic character of the copolymers and coherent results concerning orientation effects of the nematogenic groups were obtained.

Acknowledgements

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