Styrene-butadiene Rubber Synthesized by Anionic Polymerization

Mihaela-Corina Iovu[1], Selwyn Mapolie[1]*, Alina Gabriela Britchi[2]

[1]University of the Western Cape, Chemistry Department, Private Bag X17, Bellville 7535, Republic of South Africa

[2] National High Field NMR Laboratory, Institute of Organic Chemistry, Romanian Academy, 202 B Splaiul Independentei, 71141-Bucharest, Romania.

SUMMARY: In this paper we report on the copolymerization of styrene with butadiene in cyclohexane as solvent. Some experiments were also done using toluene as a solvent in order to check the influence of this solvent on the polydispersity index of the copolymers obtained. n- Butyllithium (BuLi) was used as initiator, while methyl-tert-butyl ether (MTBE) was used as an active center modifier. Reaction parameters such as polymerization temperature, the [MTBE]/[BuLi] molar ratio and the nature of solvent were studied in relation to their effects on the copolymerization rate, the randomness of the polymer and the microstructure of the butadiene units incorporated.

Introduction

Two methods are generally used for the synthesis of styrene-butadiene rubber (styrene-butadiene random copolymers): emulsion copolymerization (radical copolymerization) and solution copolymerization (anionic copolymerization)[1]. The latter offers some advantages over the former[1].

In hydrocarbon solutions the alkyllithium-initiated copolymerization of styrene with butadiene are unusual and provide an example of the importance of crossover reactions relative to homopolymerization reactivity in determining copolymer composition. The homopolymerization rate constants for styrene and butadiene are $1.6 \times 10^{-2}(\mathrm{L/mole})^{1/2}$ and, 2.3×10^{-4} $(\mathrm{L/mole})^{1/4}$ respectively. However, it is observed that butadiene is incorporated into the copolymer more rapidly than styrene. Because of this and the fact that these are living polymerizations, copolymerization of mixtures of a diene and styrene in hydrocarbon solvent yields an unusual type of structure with compositional heterogeneity incorporated intramolecularly along the polymer chain. This type of copolymer composition is described as either a tapered block copolymer or a graded block copolymer.

CCC 1022-1360/00/$ 17.50+.50/0

From a phenomenological perspective, for a typical copolymerization of styrene and butadiene (25/75, mole/mole), the solution is initially almost colorless, corresponding to the dienyllithium chain ends, and the rate of polymerization is slower than the homopolymerization rate of styrene. After approximately 70 – 80 % conversion, the colour of the solution changes to orange-yellow, which is characteristic of styryllithium chain ends. At the same time, the overall rate of polymerization increases[2].

Random copolymers with 1,2-addition as the main structural feature are obtained if a small amount of polar modifiers is added in the system.

Experimental

Materials

The purification of reagents was done carefully because this system is very sensitive to impurities. The description of purification methods have been reported elsewhere[1].

Polymerization

The copolymerization of styrene with butadiene was carried out in a specially designed apparatus. This consisted of two main parts. Part **A** of the set-up is a special type of polymerization reactor consisting of eight vials and a distribution system, while part **B** is used for the preparation of the polymerization mixture[1].

Polymer characterization

The molecular masses were calculated from GPC data obtained using a Waters/Millipore 244 system employing 4 x 30 cm Waters Ultrastyragel mixed bed columns with a refractive index detector. The styrene content of the obtained styrene-butadiene copolymers was determined using UV-VIS Spectra employing the Meehan's method[3,4]. The spectra were recorded in the range 240-330 nm, on a Specord M 40 (Carl Zeiss Jena) spectrometer, using chloroform as a solvent. The microstructures of the butadiene units in the obtained copolymers were deduced from their IR spectra[5]. The IR spectra were measured using a Perkin-Elmer 1720-X Fourier transform infrared spectrometer fitted with a mercury cadmium telluride (MCT) detector operating at 77 K. Copolymer films were cast onto KBr discs from chloroform solutions.

The randomness of the styrene-butadiene copolymers was determined from the IR, ^{1}H-NMR and ^{13}C-NMR spectra[1]. ^{1}H-NMR and ^{13}C-NMR spectra of samples were recorded on a Bruker Avance 400 MHz spectrometer.

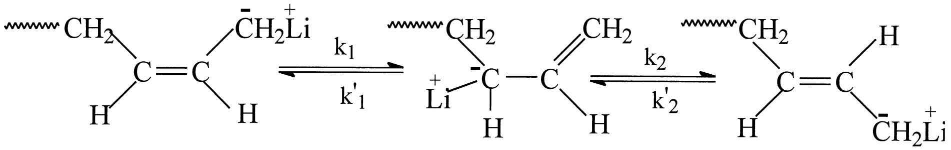
Results and Discussions

For both styrene and butadiene, the dependencies of –lg(1-conversion) on the polymerization time are linear, which indicates first partial reaction orders for the two monomers[1].

The reactivity ratios for styrene and butadiene were calculated for three different copolymerization processes[1] (at 50^{0}C for two different [MTBE]/[BuLi] molar ratios and at 60^{0}C), using the extended method proposed by Kelen and Tudos[6]. The styrene reactivity ratio is higher at higher [MTBE]/[BuLi] molar ratio[1].

Microstructure of copolymers at different conversions

The microstructure of the butadiene units incorporated into the styrene-butadiene copolymer also depends on conversion (Fig. 1). It is observed that as the conversion increases, the cis-1,4 content decreases and the trans-1,4 content slowly increases. The dependence of the vinyl content on conversion is quite weak. A possible explanation for the data presented in Fig. 1 may be given by taking into account the isomerization reaction of end cis-1,4 units to trans-1,4 units through a vinyl transition state[7,8] (Scheme 1) :



Scheme 1

If the propagation rate is much higher than the isomerisation rate, 1,4-cis units should prevail throughout the copolymer structure. If the propagation rate is close to the isomerisation rate and $k_2 >> k_1$ and $k_2 >> k_2'$, the vinyl content is less than the trans-1,4 content. Finally, if $k_2 \approx k_1$ and $k_2 \approx k_2'$, the cis-1,4 to trans-1,4 transformation rate is comparable with that of cis-1,4 to vinyl units transformation[9]. It can be seen from the data shown in Fig. 1 that the propagation rate decreases due to the lowering of the monomer concentration and to the fact that the diffusion of active chain ends is hindered because of the higher viscosity of the system. Therefore the cis-1,4 content gradually decreases and in the meantime the trans-1,4 units content increases because the isomerisation reaction rate is not influenced by the diffusion process. Also, a part of the isomerisation reactions may lead to formation of vinyl units.

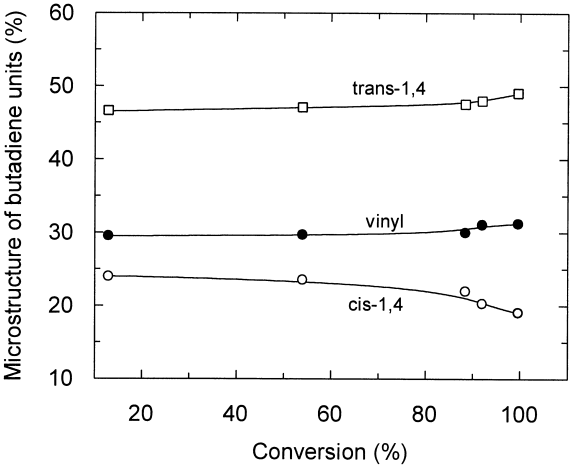


Fig.1. The dependence of the microstructure of the butadiene units on conversion for the copolymerization of butadiene and styrene initiated with the BuLi-MTBE initiator system. Polymerization conditions: [B]=1.7 mol/l; [S]=0.3 mol/l; [Monomers]=15%, [MTBE]/[BuLi]=45, [BuLi]=1.7 x 10^{-4} mol/l, polymn temp.=40°C.

Influence of [MTBE]/[BuLi] molar ratio

The influence of the [MTBE]/[BuLi] molar ratio on the copolymerization rate, microstructure of the butadiene units and the randomness of the obtained copolymers was studied[1]. The results of preliminary experiments showed that only at a [MTBE]/[BuLi] molar ratio of higher than 10, did the styrene butadiene copolymers show a random distribution of the units in the macromolecular chain. The copolymerization rate increases as values of the [MTBE]/[BuLi] molar ratio increase in the range 7 < [MTBE]/[BuLi] < 40[1]. At [MTBE]/[BuLi] > 40 the colpolymerization rate begins to decrease slightly[1].

By increasing the [MTBE]/[BuLi] molar ratio the content of the vinyl butadiene units increased (Fig.2).

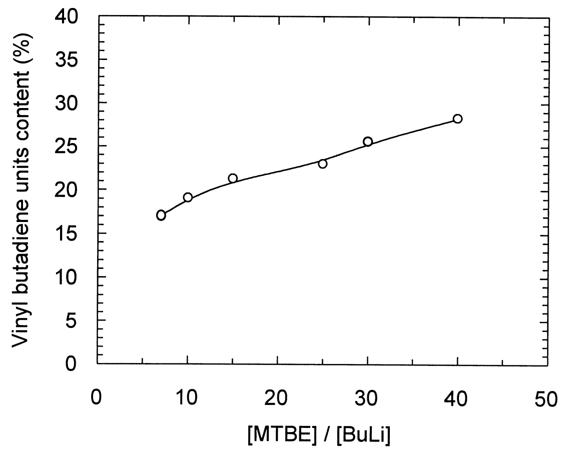


Fig. 2. The dependence of the vinyl butadiene content on the [MTBE]/[BuLi] ratio for the copolymerization of styrene with butadiene. Polymerization conditions: [B]=1.5 mol/l; [S]=0.17 mol/l; [Monomers]=15%, [BuLi]=1.5×10^{-4} mol/l, polymn. temp.=60°C.

Influence of copolymerization temperature

The copolymerization reaction rate increases as the polymerization temperature is increased. However, a more important effect of increased temperature is the lowering of the copolymers randomness. Thus, at a polymerization temperature of 60°C (or higher), small blocks of styrene units were detected by IR and ^{1}H-NMR at high conversions (over 90%). In the ^{1}H-NMR spectra of the copolymers synthesized at 60^{0}C and at [MTBE]/[BuLi] = 25, the signal at 6.6 ppm is due to the styrene triads in the copolymer chain (Fig.3).

This signal does not appear in the copolymers synthesized at 50^{0}C and [MTBE]/[BuLi] = 25 (Fig.3). A signal at 6.6 ppm was observed for all the copolymers synthesized at 10<[MTBE]/[BuLi]< 40 and 60^{0}C but was not observed for the copolymers synthesized at the same [MTBE]/[BuLi] but at 50^{0}C or less.

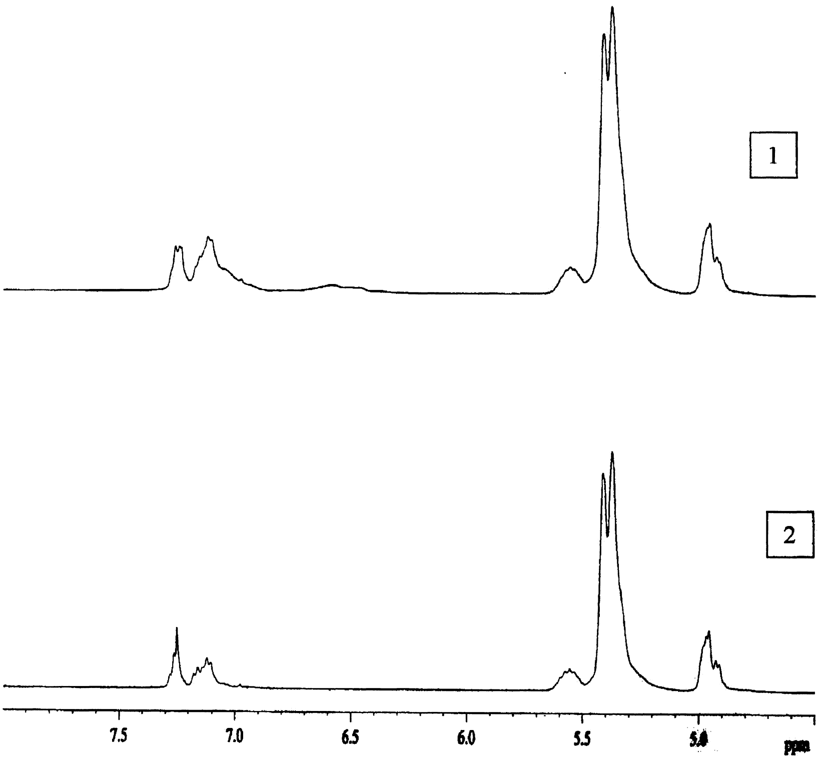


Fig.3. ^{1}H-NMR spectra of styrene-butadiene copolymers synthesized at 50^{0}C and 60^{0}C.
(1) Styrene - butadiene copolymer synthesized at 60^{0}C and [MTBE]/[BuLi] = 25;
(2) Styrene - butadiene copolymer synthesized at 50^{0}C and [MTBE]/[BuLi] = 25.

For [MTBE]/[BuLi] molar ratios higher than 10, the influence of the polymerization temperature on the copolymers randomness may be explained on the basis of the equilibrium established between complexed and uncomplexed MTBE-active centers. Depending on the value of the polymerization temperature, this equilibrium is shifted to the complexed form at lower temperatures or to the uncomplexed form at higher temperatures. Thus, at a polymerization temperature of 60°C (or higher), the propagation reaction by uncomplexed active ends will be favored.

Influence of the solvent

For the copolymerization reactions conducted in cyclohexane, the number-average molar mass linearly increases as the conversion increases, which is a proof for the absence of transfer reactions. In the case of toluene as solvent, the dependence is linear only up to 45 % conversion[1]. The reason for this behavior is based on the possibility of transfer reactions with toluene.

The polydispersity index (M_w/M_n) is almost independent of conversion in the case of copolymers synthesized in cyclohexane, while in the case copolymers synthesized in toluene the polydispersity index increases with conversion (Fig.4).

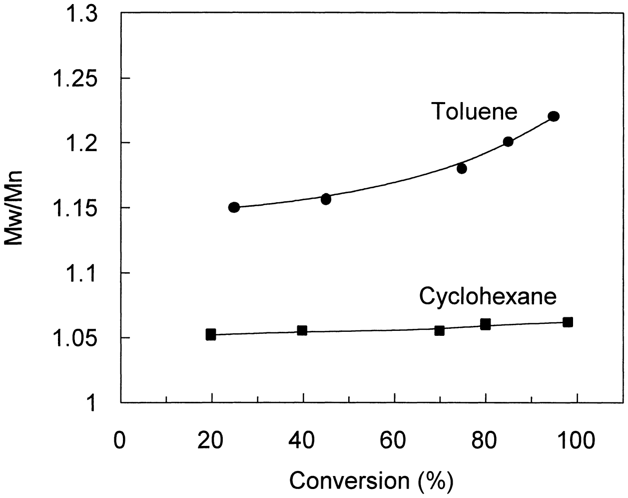


Fig.4. Dependence of polydispersity index of the butadiene styrene copolymers on conversion using MTBE-BuLi initiator system in (•) toluene, (■) cyclohexane. Polymerization conditions: [B]=1.5 mol/l; [S]=0.17 mol/l; [Monomers]=15%, [MTBE]/[BuLi]=23, [BuLi]=2.6 x 10^{-4} mol/l, polymn. temp.=50°C

This behavior for the case of copolymerizations carried in toluene can be attributed to the increase of contribution of transfer reactions with increasing of conversion.

Conclusions

Random styrene-butadiene copolymers may be obtained by anionic polymerization using methyl tert-butyl ether as modifier. The randomness of the synthesized copolymers depends mainly on the copolymerization temperature and the [MTBE]/[BuLi] molar ratio. Increasing the [MTBE]/[BuLi] molar ratio will lead to an increase of the vinyl butadiene content. No transfer and termination reactions were detected in cyclohexane but transfer reactions were detected when toluene was used as solvent. The styrene-butadiene copolymers synthesized in cyclohexane exhibit very narrow molecular weight distributions (i< 1.1), while in toluene the molecular weight distributions are between 1.1 and 1.25.

References

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