

Stability of the Chain Structure of a Styrene–Isoprene Diblock Copolymer during the Hydrogenation by Diimide

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SYNOPSIS

Olefinic double bonds of a model styrene–isoprene diblock copolymer were hydrogenated using diimide (generated by a thermal decomposition of *p*-toluenesulfonyl hydrazide). The presence of byproducts and/or main-chain structural alterations (e.g., degradation or cross-linking), as a possible side effect of this polymer analogous reaction, was checked by NMR spectroscopy, elemental analysis, static and dynamic light scattering, and GPC. A twofold concentration of Irganox 1010 antioxidant in the reaction mixture (as compared to the original reported procedure) seems to inhibit the formation of byproducts as well as to prevent any alterations on the macromolecular level. No reactions of isoprene monomer units (other than the addition of hydrogen atoms) and no changes in molar-mass distribution of the substrate were detected by the methods used.

INTRODUCTION

It is the aim of most block-copolymer syntheses to obtain a product having a molar-mass distribution as narrow as possible. On the other hand, in one of our previous papers,¹ we described a special anionic synthesis of a model styrene–isoprene diblock copolymer with intentionally broadened molar-mass distributions of both blocks. Such relatively broad distributions were necessary to make the parameters of chemical heterogeneity sufficiently high and, accordingly, their determination by light scattering sufficiently accurate. To obtain the heterogeneity parameters by an alternative method, a preparative fractionation of this “broad” copolymer was suggested,² with the use of a binary demixing-solvent system.^{3,4} Prior to any attempt at fractionation, the olefinic C=C bonds of the isoprene blocks should, if possible, be completely and specifically saturated because aliphatic chains are much more resistant than are their olefinic precursors toward undesirable chemical changes (such as cross-linking or degradation occurring during a prolonged exposure to elevated temperatures at such fractionation).

In this study, hydrogenation by diimide (diazene, N₂H₂), generated *in situ* by a thermal decomposition of *p*-toluenesulfonyl hydrazide (TSH), was applied. This reduction method was invented simultaneously by Harwood et al.⁵ and Mango and Lenz⁶ and was soon used in various studies on polydienes and their copolymers^{7,8} because of its efficiency and instrumental simplicity. However, undesirable side reactions were soon recognized, such as the addition of fragments of decomposed TSH to a certain portion of the olefinic double bonds^{5,6,9} or the *cis/trans* isomerization of unreacted double bonds.¹⁰ This was a serious drawback that had limited the use of the method until Wang et al.¹¹ discovered that the presence of an efficient antioxidant, e.g., Irganox 1010, in the reaction mixture suppressed substantially the formation of byproducts. This discovery also enabled the researchers to prolong the reaction times and thus to reach virtually 100% conversion.^{11,12} Very little attention has been paid to possible structural alterations on the macromolecular level,^{9,11} such as degradation or cross-linking, resulting in a change of overall molar-mass and composition distribution of the substrate.

It is obvious that, if the heterogeneity data obtained for our starting unsaturated copolymer from a series of light-scattering measurements¹ are to be compared with those from the fractionation of its

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hydrogenated analog, it must be guaranteed that the hydrogenation procedure does not affect the chain architecture to any perceivable degree. The most rigorous criterion of presence or absence of such undesirable main-chain alterations would be a comparison of experimentally determined two-dimensional distribution functions of both chemical composition and molar mass before and after hydrogenation. This is, however, an extremely laborious and sometimes unfeasible task. Instead, we have compared some parameters related to this distribution as well as results obtained from GPC and light scattering. Although minor changes on the level of a monomer unit, like an addition of *p*-toluenesulfinic acid to some of the double bonds, are unimportant for our purpose, we also made an attempt to estimate their extent.

EXPERIMENTAL

The synthesis of the substrate, i.e., poly(styrene-*block*-isoprene), as well as its detailed solution characterization, are described elsewhere,¹ using the same sample code, SI-w. Unlike most reported styrene-isoprene block copolymers containing predominantly 1,4-addition structures in their isoprene blocks, SI-w contains 59% 3,4- and 9% 1,2-isomers of the isoprene units.

To check the reproducibility of the reaction, three experiments of diimide hydrogenation were carried out, starting from the same stock sample SI-w. Feed ratios and reaction conditions were identical for all three runs. The products were coded SI-w/h-1 through /h-3. We strictly followed the procedure of Hsieh and Yeh¹² (including, i.e., feed ratios, temperature, reaction times, and the regime of repeated addition of TSH to the reacting mixture), with the exception of Irganox 1010 antioxidant concentration, which was used twice as high in our experiments. Thus, we adjusted initial [C=C] to 0.055 mol/L, initial [TSH] to 0.11 mol/L, and the concentration of Irganox 1010 to 0.0008 g/mL. A xylene solution of this mixture was refluxed under N₂ with stirring for 24 h. During that time, new TSH was repeatedly added (three times) so that the final mol ratio of the total TSH to the initial C=C was 5. A reported isolation procedure was used.¹²

The species present in the reaction mixtures, i.e., TSH (Fluka), Irganox 1010 (Ciba-Geigy), and xylene (Lachema Brno, Czechoslovakia), were used as received.

¹H-NMR spectra of copolymers (both substrate and reaction products) were recorded with a PS-100 (JEOL) spectrometer at 70°C and 100 MHz, with

CCl₄ as solvent and hexamethyldisiloxane as internal standard.

The static light-scattering (SLS) measurements were carried out at 25°C with a Sofica 42 000 instrument, equipped with a He-Ne laser ($\lambda_0 = 633$ nm, the usual angular range). A 1 : 1 (v : v) mixture of freshly distilled dioxane and cyclohexane was used as the solvent. Optical clarification of solutions was performed either by direct ultracentrifugation in the scattering cells¹³ or by pressure filtration through a sintered-glass bacterial filter. Experimental data were treated by the Zimm method.¹⁴ Refractive index increment values, necessary for the evaluation, were measured with a Brice-Phoenix Model BP-2000-V differential refractometer.

The dynamic light-scattering (DLS) experiments were performed using a homodyne photon correlation spectrometer with a 96-channel correlator (constructed at the Institute; for details, see Ref. 15) and a He-Ne laser. The tetrahydrofuran solutions were thermostated to $26 \pm 0.05^\circ\text{C}$. The mass-to-number average molar mass ratio M_w/M_n was evaluated by a method described earlier,¹⁶ assuming, alternatively, logarithmic normal and Schulz-Zimm distributions of the polymer samples.

Chromatographic measurements in the GPC mode were carried out with a Spectra-Physics liquid chromatograph, consisting of SP 8100 basic instrument, SP 4200 integrator, and SP 8440 UV-VIS detector. This setup was completed with a Waters R 401 differential refractometer so that the signals from both detectors, corresponding to the same injection, could be registered simultaneously in both channels of the integrator. The phase shift between the two corresponding peak maxima was thus exactly equal to the volume of the liquid between both detectors, viz. 275 μL . The columns were packed with macroporous spherical silica gel (8 μm mean particle diameter). The calibration curves used, i.e., the log *M* vs. retention time dependencies for polystyrene standards, were virtually linear in the 10⁴–10⁶ molar-mass range. Freshly distilled dichloromethane (DCM, Lachema Brno, Czechoslovakia) was used as the mobile phase with a flow rate of 0.5 mL/min. The columns were kept at 40°C and the injection volume was 100 μL . Each sample was tested by five successive injections of its solution in DCM, and an average result was always taken for further considerations.

RESULTS AND DISCUSSION

An analysis of ¹H-NMR spectra revealed that the olefinic proton signals, present for SI-w in the range

of δ between 4.4 and 6.0 ppm (depending on the microstructure of the isoprene block), were totally absent in all three hydrogenation products (for peak assignment, see Ref. 17). (An attempt was made to determine the residual olefinic bonds [the concentration of which lies well below the sensitivity limit of NMR] by quantitative ozonolysis, but the consumption of ozone by product solutions was very low, irreproducible, and barely higher than that for the pure solvent used [CCl_4].)

The chemical composition of both unsaturated and saturated copolymers was calculated from the ratio of integrated NMR peak intensities of aromatic and nonaromatic protons. The value of the mol fraction of the styrene component for the substrate was found—within the limits of experimental error—to be identical with those for the products, viz. 0.40; because of a small difference between the molar masses of hydrogenated and nonhydrogenated isoprene monomer units, the mass fractions of styrene also were equal, i.e., 0.50 (cf. Ref. 1). Thus, no residual olefinic bonds and no overall compositional changes were detectable by NMR.

To estimate the degree of undesirable addition of the TSH fragments to the olefinic double bonds during the hydrogenation, elemental analysis of the product was carried out. In the presence of Irganox 1010, adducts of *p*-toluenesulfonic acid (TSA) are the only assumed byproducts.¹¹ If, hypothetically, all olefinic double bonds of the sample SI-w added only TSA and no hydrogen, then the product would contain 7.14 wt % of sulfur. As only traces of S were found (below the sensitivity limit of determination), those olefinic double bonds that added molecules of TSA instead of hydrogen cannot constitute more than ca. 0.6% of the total isoprene units and may thus be neglected for our purpose.

As the molar-mass polydispersity of both copolymer blocks (and thus also the chemical heterogeneity) of our SI-w sample were, intentionally, adjusted to a relatively high level by the synthesis¹ (M_w/M_n of the styrene and isoprene blocks were determined to be 1.84 and 1.4, respectively), a single measurement of SLS of both SI-w and its saturated analog yielded, generally, an apparent molar mass M^{ap} instead of the true mass-average molar mass, M_w (for theory, see, e.g., Ref. 18). However, the mixed solvent used in our SLS experiments (dioxane/cyclohexane, 1/1 by volume) was chosen so as to minimize the difference $M^{\text{ap}} - M_w$. (This may be achieved if the refractive index increment of the whole copolymer is made as high as possible and, simultaneously, the difference of the values of this quantity pertaining to respective copolymer components is minimized.)

Another reason for the use of the solvent mixture was that it dissolved not only SI-w and its hydrogenated analog but also the respective homopolymers to form molecular solutions. Preferential sorption of the mixed-solvent components (cyclohexane onto polyisoprene or hydrogenated polyisoprene and dioxane onto polystyrene blocks), though undoubtedly present, did not interfere here because both solvent components exhibited virtually equal refractive indices.

By a series of measurements in several solvents, we previously determined¹ that $M_w = 292,000$ g/mol for SI-w. From the same set of data, the value of M^{ap} could be predicted for any solvent; for the dioxane/cyclohexane mixture, we predicted that $M^{\text{ap}} = 344,000$ g/mol, which is close to the experimental value given in Table I. As expected, M^{ap} is higher than M_w , but the difference is not very large. Accordingly, the use of M^{ap} as a criterion for the comparison in Table I is justified.

The differences between the values of apparent molar mass M^{ap} (obtained by SLS measurements) of SI-w before and after hydrogenation, as well as between individual hydrogenation runs (h-1 through h-3), are smaller than the experimental error of SLS (Table I).

As we were convinced that the determination of the overall copolymer mass-to-number average molar mass ratio by the DLS measurements¹⁶ was somewhat more reliable and accurate than that by the classical combination of, e.g., SLS and membrane osmometry, we chose the former method. Its results (Table I) suggest that, with the exception of the h-1 hydrogenation run, virtually no change of the mass-to-number average molar mass ratio pertaining to this polymer analogous reaction can be observed. Also, the type of the molar-mass distribution (logarithmic normal or Schulz-Zimm), se-

Table I Results of the SLS and DLS Measurements Carried Out in a Dioxane/Cyclohexane (1/1, v/v) Mixture and in Tetrahydrofuran, Respectively

| Sample Code | $10^{-3} M^{\text{ap}}$ (SLS) (g/mol) | M_w/M_n (DLS) | |
|-------------|---------------------------------------|-----------------|-------------|
| | | Log Normal | Schulz-Zimm |
| SI-w | 325 | 1.30 | 1.30 |
| SI-w/h-1 | 297 | 1.65 | 2.00 |
| SI-w/h-2 | 319 | 1.30 | 1.30 |
| SI-w/h-3 | 314 | 1.25 | 1.25 |

M^{ap} , M_w , and M_n are the apparent, mass-average, and number-average molar masses of the polymer samples.

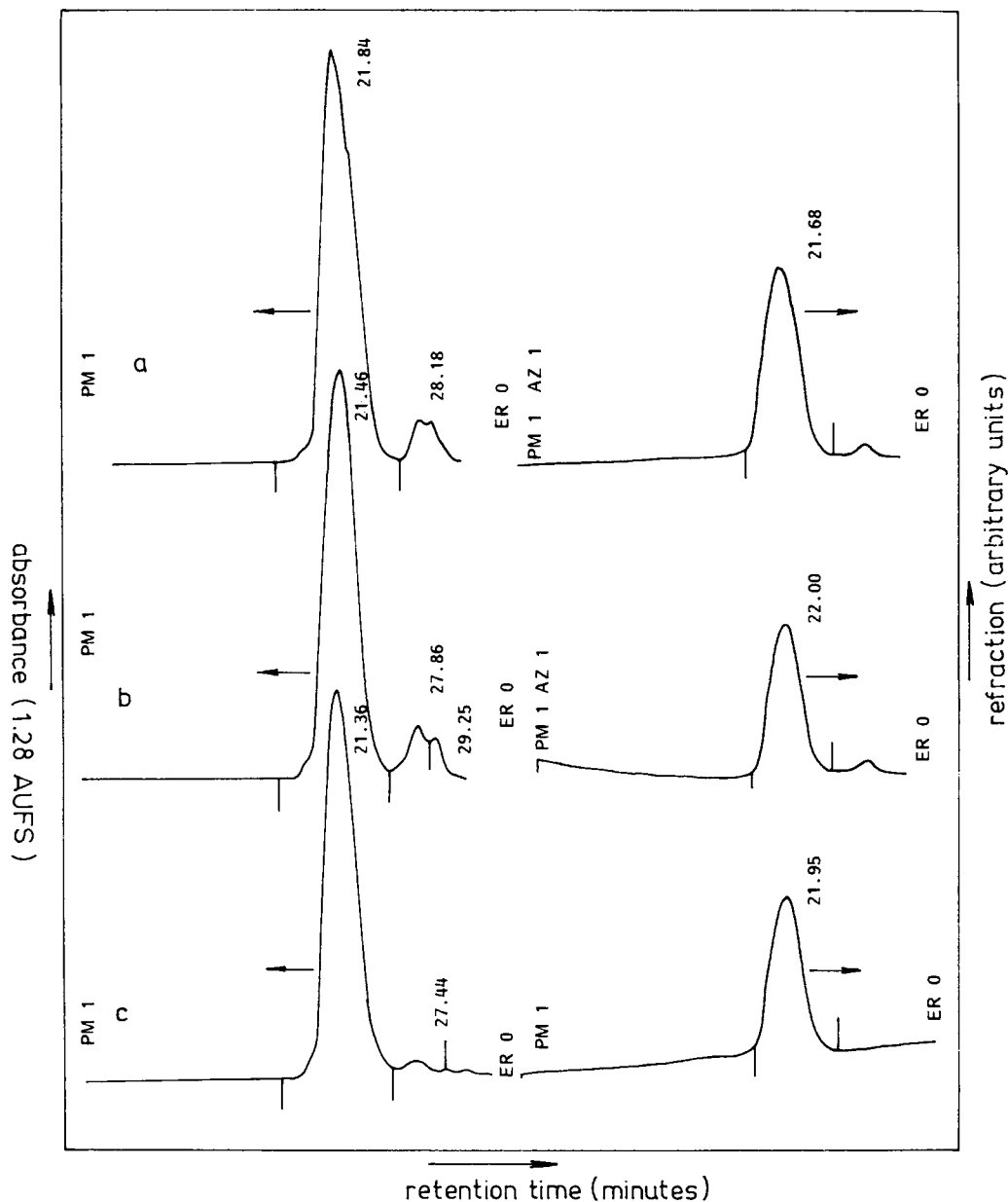


Figure 1 Examples of gel permeation chromatograms registered simultaneously by UV (left half) and refractometric (right half) detectors. (a) SI-w, (b) SI-w/h-1, and (c) SI-w/h-1 extracted by methanol.

lected as a model for the copolymers under study in order to calculate M_w/M_n for the copolymer, exhibits no effect upon this ratio (again with the exception of h-1, to be discussed below). The value of the overall M_w/M_n , determined by DLS for SI-w, is equal to that determined previously¹ by a combination of SLS and membrane osmometry (1.30).

In Figure 1, GPC responses of (a) sample SI-w, (b) sample SI-w/h-1, and (c) a methanol-extracted sample SI-w/h-1 are shown as examples. By com-

paring the retention times at the peak maxima of the original nonhydrogenated copolymers (sample SI-w before and after extraction by methanol) with those of the hydrogenated ones (samples SI-w/h-1 through /h-3 and extracted sample SI-w/h-1), we observed that the latter were slightly but reproducibly higher. According to the polystyrene/dichloromethane (DCM) calibration curve, this shift of retention times corresponds, apparently, to a decrease by 20,000–30,000 g/mol, as expressed in mo-

lar masses of polystyrene standards. We suggest, however, that this shift is caused by a decrease of hydrodynamic dimensions of the substrate after the hydrogenation and not by a possible degradation. In fact, hydrogenated samples, due to the absence of rigid C=C bonds in the backbones of their non-aromatic blocks, should behave in the GPC experiment as if their chains had apparently smaller dimensions than those of their unsaturated and thus less flexible precursor.

All curves in Figure 1, but especially (a) and (b), show minor ballast peaks in the low-molar-mass region, both in UV and refractometric detection. As these peaks had been assumed to correspond to traces of nonpolymer admixtures or impurities (e.g., the original SI-w contained a small amount of 2,6-di-*tert*-butyl-*p*-cresole, and, before the hydrogenation, a relatively large amount of Irganox 1010 was added to the reaction mixture), several samples were extracted by methanol (a solvent for the antioxidants and a nonsolvent for either of the copolymer blocks). The dramatic diminution of the ballast peaks after the extraction [as illustrated by sample SI-w/h-1 in curve (c)] seems to support this assumption. The remaining small deformation of the base line can be explained by low efficiency of the extraction. It can be concluded that the ballast peaks do not reflect the presence of any possible degradation fragments of macromolecules.

It was found that, under the given conditions, the ratio of the integrated peak areas registered by the refractometer and by the UV detector was ca. 0.41 for the nonhydrogenated samples. For saturated analogs and under identical experimental conditions, this ratio was 0.34. Although it is obvious that this ratio has no physical meaning (depending, i.e., on the detector sensitivity used), it follows from these two values that the polyisoprene units contribute to the refractive index increment of the whole copolymer in DCM more than do the units of hydrogenated isoprene. This is in good agreement with the general rule that a compound containing C=C bonds exhibits a higher refractive index than does its saturated derivative (e.g., isoprene and 2-methyl butane have n_D^{20} values of 1.4221 and 1.355, respectively). Although the assumption of additivity of refractive index increments of both copolymer blocks is realistic, no quantitative conclusions could be drawn from the GPC experimental results, mainly because no refractometric data of the system hydrogenated polyisoprene/DCM were available.

However, a comparison of the shape (width and symmetry) of the GPC peaks before and after hydrogenation suggests no detectable macrostructural

changes, such as cross-linking or chain scission, suspected to accompany the reduction process. A very small broadening of the refractometer-registered peaks (ca. 60 μ L increase of the half-width) observed after the saturation can be explained by a different degree of longitudinal spreading in the volume between the UV detector and the refractometer.

The increase of M_w/M_n from 1.3 to 1.6–2.0, detected by DLS for the h-1 hydrogenation experiment only, would mean a relatively large growth of substrate polydispersity that should definitely manifest itself by distinct broadening of the GPC peaks. This was not found. We can offer no unambiguous explanation of this inconsistency, but we suspect that the observed $M_w/M_n \geq 1.6$ is an artifact caused probably by an unknown effect during the DLS measurement. In other words, we do not doubt the reproducibility of the hydrogenation procedure, but we recommend one to be careful when using DLS for routine determination of M_w/M_n .

CONCLUSIONS

Under the conditions described by Hsieh and Yeh¹² for diimide hydrogenation, which we modified by the use of higher antioxidant concentrations, no side effects in the substrate (a diblock styrene-isoprene copolymer) were detected by the methods used, i.e., NMR spectroscopy, elemental analysis, static and dynamic light scattering, and GPC. The relatively high concentration of the antioxidant seemed to block not only the addition of sulfur-containing fragments of the reagent (*p*-toluenesulfonyl hydrazide) onto the olefinic double bonds but also the main-chain scission and/or cross-linking, though the substrate was, due to a relatively high content of pendent vinyl groups, more sensitive toward such side reactions than, e.g., commercial Kratons containing predominantly 1,4-structures.

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