Macromolecules **1994,** *27,* 6221–6222

Notes

Addition of Gaseous Carbon Dioxide to Lithium Polystyrene in Solution and in a Glassy Polystyrene Matrix

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Received December 3, 1993
Revised Manuscript Received July 25, 1994

Introduction

Solutions of lithium polystyrene react differently with carbon dioxide than the "freeze-dried" living polymer. A tentative explanation of this difference is presented here.

Carboxylation of lithium polystyrene (PSLi) solutions might be expected to proceed as a simple quantitative reaction described by scheme 1. However, the yield of the

$$\sim\sim\sim CH_2\bar{C}HPh,Li^+ + CO_2 \rightarrow \sim\sim\sim CH_2CH(Ph)CO_2Li \quad (1)$$

expected carboxylic acid is low, ~60% only, as reported by the early investigators, Wyman and co-workers,[1] who carboxylated benzene solutions of PSLi, and Mansson,[2] who performed this reaction in methylcyclohexane. The dimeric ketone, $(\sim\sim CH_2CHPh)_2CO$, 28%, and trimeric alcohol, $(\sim\sim CH_2CHPh)_3COH$, 12%, accounted for the other products of the carboxylation.

These results induced Quirk and his co-workers[3-7] to investigate thoroughly the effect of conditions prevailing during the carboxylation on its outcome. It was suspected that moisture in the introduced carbon dioxide hydrolyzes the diadduct; $(\sim\sim\sim CH_2CHPh)_2C(OLi)_2$, yielding the dimeric ketone which, on reaction with another PSLi molecule, gives the trimeric adduct, $(\sim\sim\sim CH_2CHPh)_3C(OLi)$, and eventually, after hydrolysis, the trimeric alcohol. One might expect that formation of the latter alcohol could be prevented if carboxylation is performed under vacuum conditions using meticulously purified carbon dioxide rigorously free of moisture. Indeed, as stated in the early reports of Quirk,[3,4] no tertiary alcohol was detected in the products when the process was carried out under strictly anhydrous conditions.

Continuation of these studies[5] revealed however that even under anhydrous conditions the tertiary alcohol is still produced. The alcohol was detected when six chromatographic columns were employed in the SEC, whereas the previously used device involving only three columns failed to reveal its presence. This finding is instructive, showing the need for utmost care in research concerned with these sensitive lithium compounds.

As was realized later,[5] formation of the dimeric ketone does not require hydrolysis of the dimeric adduct. The ketone may be formed by the spontaneous elimination of Li_2O described by scheme 2.

$$(\sim\sim\sim CH_2CHPh)_2C(OLi)_2 \rightarrow (\sim\sim\sim CH_2CHPh)_2CO + Li_2O \quad (2)$$

Carboxylation of Benzene Solutions of PSLi

Lithium polystyrene is dimeric in benzene solution, but a minute amount of the reactive nonaggregated Li polymers remain in equilibrium with the dimers.[8] A question arises: does carbon dioxide react with the dimeric $(PSLi)_2$, as shown by scheme 3, or with the monomeric PSLi, as depicted by scheme 4. The reaction described by scheme 3 produces a molecule of the reactive, monomeric polystyrene lithium in the vicinity of its geminate carboxylated molecule. The probability of their geminate interaction yielding the dimeric adduct (ketone) should be high, and it would be only slightly affected by the initial concentration of lithium polystyryl, contrary to the reported observations.[5] In contradistinction the unaggregated lithium polystyrene, dispersed throughout the solution, has a relatively low chance of reacting with the carboxylated polystyryl and hence the yield of the ketone would then be relatively low. In view of this argument, mechanism 4 seems more plausible than mechanism 3, although partial participation of reaction 3 in the overall process cannot be excluded. Although the aggregated (dimeric) polymers are unreactive toward their monomer,[8] they might still react with the polar carbon dioxide.

$$(\sim\sim\sim CH_2\bar{C}HPh,Li^+)_2 + CO_2 \rightarrow \sim\sim\sim CH_2CH(Ph)CO_2Li + \sim\sim\sim CH_2\bar{C}HPh,Li^+ \quad (3)$$

$$(\sim\sim\sim CH_2\bar{C}HPh,Li^+)_2 \Leftrightarrow 2\sim\sim\sim CH_2\bar{C}HPh,Li^+$$

$$\sim\sim\sim CH_2\bar{C}HPh,Li^+ + CO_2 \rightarrow \sim\sim\sim CH_2CH(Ph)CO_2Li \quad (4)$$

The carboxylation performed in a mixture of benzene and THF (75/25) led to a remarkably high yield of the acid with exclusion of the dimeric and trimeric adducts.[3] This observation seems to contradict the mechanism proposed here. Since THF dissociates the aggregated lithium polystyryls[9] and increases the concentration of the unaggregated polymers, its presence should enhance the formation of the dimeric and trimeric adducts. However, solvation of the lithium cations by THF might inhibit the association of lithiated polymers with the carboxylated ones.

The effect of the reduced pressure of carbon dioxide is trivial. The yield of the trimeric alcohol greatly increases at its low pressure. In the course of carboxylation the latter reagent (CO_2) competes with the dimeric ketone for lithium polystyrene. Decrease of $[CO_2]$ favors therefore the formation of the trimeric adduct.

Freeze-Dried Lithium Polystyrene

The reaction of carbon dioxide with the solid freeze-dried lithium polystyryl led to virtually quantitative carboxylation (~99%).[5] The investigators of this carboxylation neither inquired about nor accounted for the surprising difference in the behavior of the freeze-dried lithium polystyryl compared with its solution. Let us consider therefore this problem and try to rationalize the observations.

0024-9297/94/2227-6221$04.50/0

In a dilute benzene solution of high molecular weight lithium polystyryl the dimeric aggregates form separate, nonoverlapping coils, each containing two associated $\sim\sim\sim CH_2CHPh,Li^+$ end groups. Freezing and subsequent vacuum sublimation of benzene shrinks the coils which eventually collapse, virtually without penetrating each other,[10] into a porous mass of glassy polystyrene. Each coil then forms a cell containing two associated $\sim\sim CH_2\bar{C}HPh,Li^+$ end groups. Attention should be paid to the rate of freezing. Slow crystallization of benzene results in concentration of the polymer solution which might lead to the overlap of the coils. It is advisable, therefore, to freeze the solution rapidly to avoid the interpenetration of the coils.

Although the resulting polystyrene is below its glass temperature, i.e. in a state virtually preventing any diffusion of the whole polymer molecules, the spontaneous and reversible dissociation–association of the paired end group may still persist. The movement of the end groups by a few angstroms apart breaks their association, yielding the unaggregated polymer end group. Since the latter eventually associate, the equilibrium between the aggregated and nonaggregated polymers is established. The fraction of the cells holding at any time an unassociated pair of the end groups is low, probably less than 10^{-2}, but presumably not much lower than the fraction of the unassociated lithium polymers in a hydrocarbon solution of living polymers. The latter are the propagating species capable of reacting with the monomer as well as with carbon dioxide. However, the relaxation time of the dissociation–association process is relatively long in the solid medium, permitting the addition of two consecutively arriving molecules of carbon dioxide to the separated end groups prior to their eventual reapproachment. Such a scenario may account then for the high yield of the monomeric acid (about 99%) in the carboxylation performed in the frozen state.[5]

An alternative explanation was proposed by one of the referees of this note who favors the idea of carboxylation of the aggregated polymers. He suggests that the motion of the end groups allowing the overlap of *p*-orbitals of the first-formed carboxyl carbon with the *p*-orbitals of the carbanionic end chain is restricted in the rigid polymer matrix. Since such motion is needed for the formation of the C—C bond yielding the ketone, its prevention or slowness allows for the diffusion of the second molecule of carbon dioxide, resulting in carboxylation of the other carbanion. This explanation, somewhat similar to that offered here, requires a great degree of rigidity of the surrounding matrix. The formation of the first carboxylic group disorganizes the reacting site, and the exothermicity of carboxylation melts the surrounding matrix. Hence, the demanded rigidity seems implausible.

Conclusions

Collating all the available evidence, one concludes that the dissociation–association of aggregated polystyryllithium takes place even in the matrix of the "freeze-dried" lithium polystyrene. Such a process requires only slight movement of the polymer end groups which is quite feasible even in a glassy polymer, although diffusion of the whole polymer molecules is virtually prohibited.

The presence of unaggregated polymers in the "freeze-dried" polymers makes propagation feasible even in the glassy matrix. Hence if polymerization is observed in such a medium, this phenomenon does not manifest reactivity of the aggregates. Indeed, lack of reactivity of the aggregates in solution, revealed by the kinetics of polymerization of lithium polystyrene in hydrocarbon solvents,[8] makes it implausible to expect them to become reactive toward the monomer in the rigid medium. Some participation of the aggregates in the carboxylation of lithium polystyrene cannot be ruled out, especially in the solution process, but participation of the unaggregated polymers seems to be dominant in this process.

The lifetime of the unassociated lithium polystyryl pairs is relatively long in the glassy polystyrene, allowing for the addition of two consecutively arriving CO_2 molecules to the ends of the nonaggregated polymers prior to their reapproachment. Thus the formation of the dimeric and trimeric adducts is prevented. Another variant of the reaction mechanism, contemplated but rejected by the present writer as highly implausible, postulates the formation of a complex of carbon dioxide with the aggregated lithium polystyryl which, in turn, reacts with another molecule of CO_2. Two carboxylated lithium polystyryls would supposedly be formed by this termolecular reaction.

References and Notes

(1) Wyman, D. P.; Allen, V. R.; Altares, T. *J. Polym. Sci.* **1964**, *2*, 4545.

(2) Mansson, P. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1945.

(3) Quirk, R. P.; Chen, W. C. *Makromol. Chem.* **1982**, *183*, 2071.

(4) Quirk, R. P.; Chen, W. C.; Cheng, P. L. ACS *Symp. Ser.* **1985**, No. 282, 139.

(5) Quirk, R. P.; Yin, J.; Fetters, L. J. *Macromolecules* **1989**, *22*, 85.

(6) Quirk, R. P.; Yin, J. *J. Polym. Sci.* **1992**, *30*, 2349.

(7) Quirk, R. P.; Yin, J.; Fetters, L. J.; Kastrup, R. V. *Macromolecules* **1992**, *25*, 2262.

(8) See for review: Szwarc, M.; VanBeylen, M. *Ionic Polymerization and Living Polymers*; Chapman and Hill Publishers: London, 1993; pp 159–162.

(9) See for review: Szwarc, M.; VanBeylen, M. *Ionic Polymerization and Living Polymers*; Chapman and Hill Publishers: London, 1993; pp 157–158.

(10) The evidence for nonoverlapping of the collapsing polymer coils is provided by: Chang, L. P.; Morawetz, H. *Macromolecules* **1987**, *20*, 428.