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Extending the Lifetime of a Hydrogenation Catalyst by Removal of Lithium Alkoxide from Styrene−Butadiene Block Copolymers Using Filtration

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Introduction

The anionic polymerization of styrene and butadiene in the presence of alkyllithium catalysts to produce block copolymers has been well documented.[1−4] After an initial addition of styrene to the alkyllithium catalyst to form a polystyryl anionic intermediate, sequential addition of butadiene followed by a second charge of styrene leads to a block species **1a**, referred to as a "living" polymer due to the presence of an anionic charge of sufficient stability on the terminal chain end that can be available for further reaction (Scheme 1). This living polystyryl anion can be terminated with an alcohol such as methanol or 2-propanol to give the block copolymer **1b**. Termination with an alcohol gives lithium alkoxide as a byproduct in the polymer solution. Assembly of **1** with additional monomer blocks is also possible given sufficient stability of anion **1a**.

The versatility of the physical properties of the block copolymers **1** can be enhanced by the noble metal catalytic hydrogenation of the pendant aromatic rings, vinyl groups, and butylene groups in the polymer chain to give the fully saturated block copolymer **2** (Scheme 1). Such modifications give rise to saturated polymers with increased resistance to oxidative and thermal degradation and substantially higher T_g values compared to those of the unsaturated parent polymers.[1,5,6]

A critical parameter for the successful commercial development of a hydrogenation process is a determination of the key causes of catalyst deactivation and the demonstration of an extended lifetime of the costly noble metal catalyst.[7] Our initial work with the hydrogenation of block copolymers indicated that removal of lithium alkoxide from hydrocarbon solutions of **1b** was a critical factor in attaining a prolonged catalyst lifetime that approached commercially acceptable values. The deactivating effect of lithium alkoxides is likely due to their tendency to bind to and block access to active catalyst sites. By the judicious choice of terminating alcohol to give **1b** from **1a**, we have focused on the ability to remove lithium alkoxide from polymer streams to very low levels by simple filtration. This led to a dramatic improvement in the lifetime and activity of the hydrogenation catalyst used to produce **2**.

Scheme 1

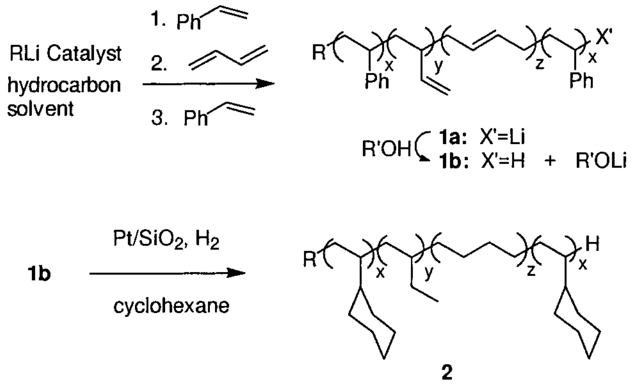

Table 1. Filtration of 15% Solutions of 1b in Cyclohexane through Membrane Filters; Comparison of 1b Terminated with *i*-PrOH vs MeOH

polymer solution	Li, ppm
1b, *i*-PrOH terminated, no filtration	37
filtered, 0.45 μm[a]	36
filtered, 0.22 μm[a]	26
filtered, 0.22 then 0.1 μm[a]	12
1b, MeOH terminated, no filtration	14
filtered, 0.45 μm[a]	nd[b]

[a] Durapore hydrophobic modified poly(vinylidene fluoride) (PVDF). [b] Nondetected at a 0.05 ppm detection limit.

Results and Discussion

Removal of Lithium by Filtration. The removal of lithium species from nonviscous low molecular weight polymer solutions by filtration has been reported.[8] Also, the use of concentrated molten salts have been reported to be effective in the removal of lithium from elastomer solutions.[9] In our work, the use of 2-propanol as the standard terminating alcohol (R′OH in Scheme 1) gave hydrocarbon solutions of **1b** in which the resulting lithium isopropoxide proved resistant to removal by filtration or adsorbents. Also, attempted aqueous extractions of the polymer solution led to intractable emulsions and large aqueous waste streams and was only marginally effective at removing lithium.

The ability of lithium isopropoxide and lithium *tert*-butoxide to form aggregates in solution is known, while such a tendency is much lower for the nonbranched lower alkoxides such as lithium methoxide.[10] Thus, by using methanol rather than 2-propanol as terminating agent for **1a**, the resulting lithium methoxide could be removed from hydrocarbon solutions by filtration through a 0.5 μm filtration unit. For laboratory filtrations the use of a membrane filter in a pressure filtration unit was also found to be effective at removing lithium to low levels.

Table 1 shows a comparison of lithium levels after filtration of an *i*-PrOH-terminated polymer with that of a MeOH-terminated one, using membrane filters. The filtration data listed in this Table show that, for a block copolymer solution that has been terminated with

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Table 2. Filtration of Methanol Terminated 15% Solutions of 1b in Cyclohexane Using Membrane Filters in a Millipore Pressure Filtration Unit

membrane	mean pore size, μm	Li, ppm
unfiltered solution		13
mixed cellulose ester[a]	8.0	5.3
	5.0	5.5
	3.0	1.7
	1.2	0.96
	0.45	0.31
	0.22	nd[b]

[a] MF-Millipore mixed nitrate and acetate esters. [b] Nondetected at a 0.05 ppm detection limit.

Table 3. Filtration of a 4400 g Methanol Terminated 15% Solution of 1b in Cyclohexane Using a 0.5 μm Prefilter Followed by a Membrane Filter

filter	Li, ppm
unfiltered solution	5.1
0.5 μm prefilter[a]	0.24
2nd 0.5 μm prefilter[a]	0.16
0.22 μm membrane[b]	0.08[c]

[a] Stainless steel random fiber cartridge. [b] 3700 g filtration sample required two membranes. [c] Detection limit is 0.05 ppm.

i-PrOH, partial removal of lithium is possible with sufficient filtration power. However, even with a 0.1 μm membrane filter, a 12 ppm Li level remained, a level deemed too high to attain multiple hydrogenation catalyst recycles. For polymer solutions terminated with MeOH, filtration through a 0.45 μm membrane was sufficient for removal of Li to a 0.05 ppm detection limit (Table 1).

An additional filtration study was carried out using mixed cellulose ester membranes with different mean pore size ratings, and the results are summarized in Table 2. A gradual reduction in lithium levels occurs with smaller pore sizes, until a nondetect level of lithium (0.05 ppm limit) was attained with a 0.22 μm membrane. Generally rapid filtration rates were attained with 8.0 and 5.0 μm membranes, which removed about 60% of the lithium. However, with smaller pore sizes the membranes plugged more quickly, which required installation of a fresh membrane.

A more optimal approach to obtaining low lithium levels along with rapid filtration rates is summarized in Table 3 and was obtained by carrying out a prefiltration through a 0.5 μm stainless steel cartridge, followed by filtration through a 0.22 μm membrane. A second filtration through the 0.5 μm filter also showed a small additional reduction of lithium levels. The 0.5 μm random fiber cartridge was effective at removing lithium to <1 ppm and served as an effective guard for the membrane. This approach gave polymer solutions having lithium levels below 0.1 ppm and allowed for the treatment of much larger volumes of polymer solution before change out of the membrane was required. In this manner, multikilogram quantities of polymer solution could be routinely treated to remove lithium to very low levels.

Effect on Hydrogenation Catalyst Lifetime. The effect on activity and lifetime of a platinum hydrogenation catalyst supported on wide pore silica extrudates[5] is shown in Table 4. A fresh charge of catalyst was used for the initial run for each set of feeds; the catalyst was reused between runs within a set. The table shows the time required for the total mass of hydrogen fed to the reactor to reach 5 and 5.5 g. As the catalyst deactivates, the rate of hydrogen consumption slows. As a result, the time taken before 5.5 g of H_2 is consumed becomes longer, especially for the final 0.5 g.

Table 4. Effect of Lithium Level on Hydrogenation Catalyst Activity As Measured by Rate of Hydrogen Consumption during Preparation of 2

	polymer solution **A**[a] 10 ppm of Li		polymer solution **B**[b] 0.7 ppm of Li	
run[c]	hours to 5 g of H_2	hours to 5.5 g of H_2	hours to 5 g of H_2	hours to 5.5 g of H_2
1[d]	0.98	1.38 (98.3%)[f]	1.38	1.88 (98.1%)[f]
2[e]	1.98	2.82 (98.2%)	1.67	2.27 (99.2%)
3[e]	3.50	4.98 (96.2%)	1.68	2.35 (99.2%)
4[e]	4.32	6.20 (98.1%)	1.80	2.52 (98.6%)

[a] Polymer solution **A:** block copolymer **1b**, 15% in cyclohexane, 2-propanol terminated, treated with activated alumina and 0.5 μm filtration through a random fiber stainless steel filter cartridge. [b] Polymer solution **B**: same polymer and treatment as **A**, but termination step was with MeOH. [c] Hydrogenation conditions: see text and ref 5. [d] Fresh catalyst. [e] Reused catalyst from previous run. [f] Numbers in parentheses refer to % hydrogenation measured by UV–vis spectroscopy. See text and ref 5.

The runs with a polymer solution containing a lithium level of 10 ppm show a substantial decrease in hydrogenation rate with additional runs and an increasing time to consume the final 0.5 g. Conversely, the runs performed with polymer solution from which the lithium level has been reduced to <1 ppm show a dramatic improvement in catalyst activity upon recycle of the catalyst in runs 2–4 (Table 4).

Conclusions

Identifying causes of catalyst deactivation and developing methods of removal of poisons are key aspects of process development for commercializing a catalytic process.[11] This is especially critical where a noble metal catalyst is used, and disposal of deactivated catalyst is prohibitively expensive. In our work with the hydrogenation of block copolymers of styrene and butadiene derived from anionic polymerizations, we have found that the propensity for lithium to accumulate on the noble metal catalyst leads to rapid deactivation. This effect will no doubt exist for a wide range of metal catalysts on supports and thus may represent a general problem where feed streams are derived from anionic polymerizations. The unlikely prospects of easily removing a metal contaminant from the spent catalyst has led to a filtration approach that can remove lithium from a feed stream to very low levels (0.05 ppm) and a demonstrated dramatic improvement in the lifetime and activity of the hydrogenation catalyst. Such an approach to a feed stream treatment represents an attractive alternative to other processes such as aqueous extractions that produce large quantities of waste streams requiring extensive treatment.

Experimental Section

General. Cyclohexane, styrene, and butadiene were obtained from commercial sources and purified by passage through a column of activated A2 alumina (Daniel Bowers Co.) to remove inhibitors and traces of moisture. The initiator *s*-BuLi was obtained from Aldrich as a 1.3 M solution in cyclohexane and used without further treatment or purification. Solutions of **1** were prepared in a 2 gal jacketed autoclave using standard anionic polymerization techniques.[2,12] Hydrogenations of block copolymers with a platinum catalyst on silica support, along with the catalyst preparation, have been reported elsewhere.[5]

Filtration of Lithium Methoxide from Polymer Solutions. The polymer solutions as obtained from the anionic reactor after termination with methanol were filtered in a Millipore 142 mm pressure filtration system obtained from Fisher Scientific. Membranes were also purchased from Fisher. A typical polymer solution volume of 300−400 mL was filtered before changing to a fresh membrane. An initial N_2 pressure of 10 psig was used, with gradual ramping of the pressure to 70 psig near the end of the filtration. A prefiltration procedure involved the pumping of a polymer solution using a peristaltic pump through a 10 in. random fiber stainless steel filter cartridge rated at 0.5 μm and purchased from Flowtech Corp. of Kalamazoo, MI. *Caution: metal filtration units should be properly grounded inside a well-ventilated fume hood to prevent ignition of flammable solvents from static discharge.*

Lithium Analysis. The polymer samples were prepared for analysis by digesting a 0.5 g portion of polymer solution using a sulfuric−nitric acid digestion procedure on an automated robotic system.[13] The solutions were allowed to cool, diluted to 25 mL with deionized water, and analyzed for lithium levels using inductively coupled plasma (ICP) emission spectrometry.[14]

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