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Hydrocarbon-Soluble Sulfonating Reagents. Sulfonation of Aromatic Polymers in Hydrocarbon Solution Using Soluble Acyl Sulfates

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ABSTRACT: Previously, we reported that some types of olefin polymers and their small-molecule models were unexpectedly resistant to sulfonation in hydrocarbon solvents. This substantial reactivity difference between chlorinated and hydrocarbon solvents was attributed to the solubility characteristics of the sulfonating agent. Aromatic polymers such as polystyrene are inherently less reactive than olefin polymers and are even more resistant to sulfonation in hydrocarbon solution. We postulated that hydrocarbon-soluble acyl sulfates, unlike acetyl sulfate, would be efficient and rapid reagents for the sulfonation of polymers that are unreactive, and this has been substantiated. Even small improvements in hydrocarbon solubility were found to be beneficial, and completely homogeneous sulfonation was possible with longer chain acyl sulfates. As a result, polystyrene was sulfonated effectively in cyclohexane solution. Long-chain phosphate ester–sulfur trioxide complexes were also soluble in cyclohexane and are suitable reagents for completely homogeneous sulfonation.

Introduction

Homogeneous sulfonation offers some potential utility of both process control and product uniformity. Small-molecule sulfonations sometimes utilize sulfuric acid, oleum, or liquid SO_2 as a mutual solvent for the substrate and sulfonating reagent, but this is not generally convenient with hydrocarbon polymers.

Polystyrene has been sulfonated homogeneously in chlorinated solvents such as dichloroethane by using triethyl phosphate–sulfur trioxide complexes.[2-4] Recently, sulfonation of polystyrene in cyclohexane utilizing H_2SO_4 catalyzed by Ag_2SO_4 has been proposed[5] as an improvement over heterogeneous sulfonation using 100% sulfuric acid. However, there are no good procedures for totally homogeneous sulfonation of polystyrene in a hydrocarbon such as cyclohexane.

We have been studying the sulfonation chemistry of some small-molecule models of EPDM rubbers using acetyl sulfate as the reagent.[6] In the course of these studies we observed that less reactive EPDM rubbers or their small-molecule models were not reactive in hydrocarbon solution using acetyl sulfate reagent. The extremely low reactivity of EPDM rubbers containing dicyclopentadiene or 1,4-hexadiene as the termonomer is in marked contrast to ethylidenenorbornene-containing EPDM, which sulfonates rapidly in hydrocarbon solution. These observations were rationalized by means of model studies which showed that many different olefin types are sulfonated rapidly in methylene chloride in contrast to hexane or pentane solution, wherein only the most reactive olefins are sulfonated. The solvent effect was traced to the low solubility of acetyl sulfate in hydrocarbon solution. Only olefins with very high specific reaction rates could be sulfonated effectively in hydrocarbon solvent where the reagent was in very low concentration; however, all of the different olefin types were extremely reactive under similar conditions using CH_2Cl_2 solvent where the reaction was homogeneous.

Recent interest in lightly sulfonated polystyrene ionomers prompted us to consider the possibility of a hydrocarbon solution process. The effect of homogeneous sulfonation demonstrated with olefin polymers should be even more significant with less reactive aromatic polymers. Indeed, Makowski[7] found that the reaction of acetyl sulfate with polystyrene, which was facile in dichloroethane, was

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Table I
Sulfonation of Polystyrene in Cyclohexane Solution (50 °C)[a]

reagents[b]	method[c]	mequiv/100 g of polymer		
		theory	titration	S microanal.
acetic anhydride–H_2SO_4	in situ	36.4	6.92	6.86
acetic acid–SO_3	premix	36.4		4.52
lauric acid–SO_3	premix	36.4	20.4	24.0
stearic acid–SO_3	premix	36.4	19.7	20.7

[a] 100 g of Styron 666/500 mL of cyclohexane. [b] [Acid]:[SO_3] = 1.6:1, 37.5 mequiv of sulfonating reagent/100 g of polymer, added in 100 mL cyclohexane. [c] Reaction time, 1 h.

ineffective in cyclohexane, but the reason for this was not understood at the time. In light of our recent observations it is reasonable that aromatics which are less reactive than olefins should have low reactivity toward acetyl sulfate in hydrocarbon solvents. This application of the insight gained from our model studies has enabled us to achieve the facile homogeneous sulfonation of aromatic polymers in hydrocarbon solution.

Results and Discussion

Preformed Acyl Sulfates. The failure to achieve effective sulfonation of polystyrene in a hydrocarbon medium is predictable in light of the fact that the aromatic nucleus is considerably less reactive toward sulfonation than the least reactive olefins. In fact, olefins can be sulfonated selectively in aromatic solvents without involving the solvent. If some of the less reactive olefins will not sulfonate in hydrocarbon media, it should not be surprising that aromatics would also be unreactive.

Our previous model studies predicted that soluble sulfonating reagents would change this situation. There are a number of applications in which polymer sulfonation in oils or other paraffinic media would be desirable, especially if the solution of the modified polymer could be utilized directly. In the case of sulfonated polystyrene, elimination of chlorinated solvent would be desirable. In addition to environmental problems (carcinogenic activity of chlorinated hydrocarbons), there are economic and technical considerations that make an all-hydrocarbon process preferable. The demonstration of an effective all-hydrocarbon process for polystyrene would also have important implications for other polymers that may be more reactive than polystyrene but are still not sufficiently reactive to be suitable for sulfonation in hydrocarbon media.

Polystyrene itself has limited solubility in paraffinic solvents; however, some cycloparaffins like cyclohexane can be utilized to dissolve polystyrene. Cyclohexane is a Θ solvent for polystyrene and the polymer is quite soluble in warm cyclohexane (50 °C) but comes out of solution on cooling. The sulfonations in this study were conveniently conducted at 50 °C using cyclohexane solutions of polystyrene.

Experiments in which higher molecular weight fatty acids were dissolved in cyclohexane and treated with liquid SO_3 ([acid]:[SO_3] = 1.6:1) gave encouraging results. Sulfur trioxide, which was insoluble in cyclohexane, dissolved rapidly in the presence of certain carboxylic acids to form a homogeneous solution at ambient temperature. Both lauric (C_{12}) and stearic (C_{18}) acids gave soluble reagents while acetic acid did not.

Acetyl sulfate is commonly generated by the reaction of acetic anhydride with sulfuric acid either in situ or by premixing the reagents and adding them to the polymer solution. Acetyl sulfate can also be generated by reacting acetic acid with sulfur trioxide. This procedure cannot be carried out in situ since SO_3 would react directly with the polymer, causing charring, gelation, etc. Similarly, higher molecular weight acids also react with SO_3 to give acyl sulfate, and we find that some of these can be very soluble in hydrocarbon solvents. This is consistent with the fact that some long-chain alkylbenzenesulfonic acids which we examined could also dissolve in cyclohexane.

Table II
Sulfonation of Polystyrene in Cyclohexane with Soluble Lauroyl Sulfate (50 °C)

reagent[a] mequiv of lauroyl sulfate/100 g of polystyrene	mequiv of sulfonation/100 g of sulfonated polymer		
		anal.	
	theory	titration	S microanal.
10	9.92	1.0	1.9
15	14.8	3.0	3.4
20	19.7	9.0	11.5
30	29.3	14.0	15.0
40	38.8	23.7	23.9
50	48.1	25.6	26.8
60	57.2	33.7	32.7
80	75.2	47.6	47.7
100	92.6	59.1	59.3
200	172.4	100.8	98.6
300	241.9	142.0	140.7

[a] 1.6 mol of lauric acid to 1.0 mol of SO_3; reaction time, 1 h.

$$(CH_3CO)_2O + H_2SO_4 \rightarrow CH_3COOSO_3H + CH_3COOH \tag{1}$$

$$CH_3COOH + SO_3 \rightarrow CH_3COOSO_3H \tag{2}$$

$$RCOOH + SO_3 \rightarrow RCOOSO_3H \tag{3}$$

The effectiveness of the sulfonating ability of the acyl sulfate reagents was quite dramatic. Acetyl sulfate generated either from sulfuric acid and acetic anhydride (in situ) or from acetic acid and sulfur trioxide in cyclohexane gave very poor results. In fact, in the latter case the acetyl sulfate precipitates from cyclohexane as a viscous liquid, which is difficult to transfer. By contrast, the substitution of lauric or stearic acid for acetic acid gave very effective homogeneous sulfonation of the polystyrene. The product was isolated as the free acid and analyzed by titration and sulfur microanalysis. Generally, good agreement was obtained between the two analytical methods (Table I).

Examination of the effect of sulfonating reagent concentration on conversion by combining soluble lauroyl sulfate solutions in cyclohexane with polymer in cyclohexane shows a linear response to increasing reagent. Table II describes the results of adding from 10 to 300 mequiv of lauroyl sulfate dissolved in 100 mL of cyclohexane at ambient temperature to 100 g of polystyrene dissolved in cyclohexane (500 mL) at 50 °C. The polymers were recovered by precipitation from excess isopropyl alcohol and dried in vacuo (50 °C).

Apparently, lauroyl sulfate is quite effective at sulfonating polystyrene over a broad range of sulfonation levels. For low sulfonation levels we observe that plotting milli-

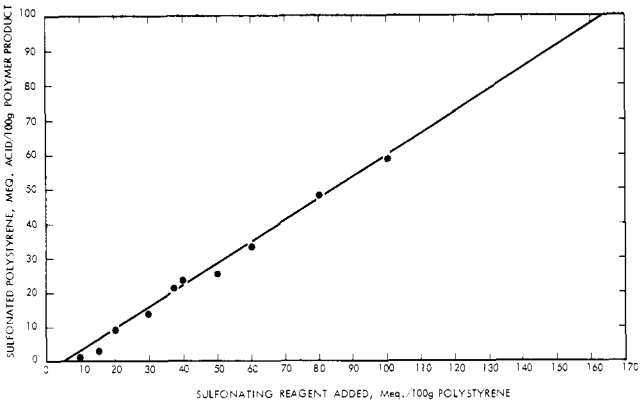

Figure 1. Lauroyl sulfate sulfonation of polystyrene in cyclohexane, 50 °C.

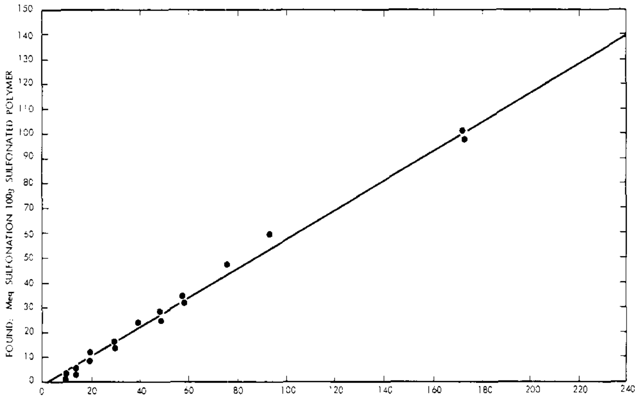

Figure 2. Lauroyl sulfate sulfonation of polystyrene in cyclohexane, 50 °C.

equivalents of sulfonating reagent per 100 g of polymer against milliequivalents of sulfonic acid per 100 g of product gives a linear relationship (Figure 1). However, at higher sulfonation levels, where the mequivalents per 100 g of polystyrene is significantly different from mequivalents per 100 g of sulfonated polymer at 100% efficiency, the abscissa must be adjusted for this difference (Figure 2).

The solubility of the sulfonated product in the hydrocarbon solvent is another consideration. If we wish to have a homogeneous process, both the sulfonating reagent and the product polymer must remain soluble. As expected, the solubility of the product diminishes with increasing sulfonation. Utilizing up to 60 mequiv of reagent per 100 g of polystyrene gave homogeneous and very tractable cements. Above this level solutions became increasingly more viscous, and it was difficult to discern whether the polymer was completely soluble. The recovered products were soluble in toluene–methanol, even at 300 mequiv of reagent, indicating that no gelation had occurred. The carboxylic acid byproduct was observed to play an important role in solvating the sulfonated polymer and is a cosolvent for the polymer. Fortunately, the carboxylic acid concentration increased with increasing sulfonate level, thereby aiding the solubility of the product as its polarity became higher.

The possibility of using lauric acid as a phase-transfer catalyst was considered. Since acetyl sulfate is conveniently generated from acetic anhydride and sulfuric acid, an attempt was made to determine whether the presence of lauric acid would improve the sulfonation efficiency. If insoluble acetyl sulfate equilibrated rapidly with lauric acid to produce soluble lauroyl sulfate, then lauric acid should catalyze the sulfonation of polystyrene by acetyl sulfate.

Table III
Lauric Acid as a Phase-Transfer Catalyst

mequiv/100 g of polystyrene			anal. (mequiv/100 g of product)	
H_2SO_4	acetic anhydride	lauric acid	titration	S microanal.
37.5	60	60[a]	5.61	8.58
37.5	60	60[b]		7.80
37.5	60		6.92	6.86

[a] Lauric acid and acetic anhydride dissolved in polymer cement prior to H_2SO_4 addition; 100 g of polystyrene in 500 mL of cyclohexane; 50 °C for 1 h. [b] Lauric acid added after acetyl sulfate was generated in situ.

Unfortunately, the addition of lauric acid to acetyl sulfate had no effect. Combining the lauric acid with acetic anhydride in the polymer cement prior to adding sulfuric acid or adding lauric acid after acetyl sulfate was generated in situ did not improve the sulfonation (Table III). We suspect that the very low solubility of acetyl sulfate contributes to the very slow equilibration with soluble lauric acid.

$$CH_3COOSO_3H + C_{11}H_{23}COOH \rightarrow C_{11}H_{23}COOSO_3H + CH_3COOH \quad (4)$$

Of course, acetic anhydride could be heated with lauric acid to produce first the mixed anhydride and finally lauric anhydride.

$$(CH_3CO)_2O + 2C_{11}H_{23}COOH \rightarrow CH_3CO\text{-}O\text{-}OCC_{11}H_{23} + CH_3COOH \rightarrow (C_{11}H_{23}CO)_2O \quad (5)$$

This is a well-known method for the production of higher anhydrides but requires the distillation of acetic acid to drive the equilibrium. We will discuss the use of higher molecular weight anhydrides with H_2SO_4 shortly.

Examination of the solubility of acyl sulfates generated from normal acids in cyclohexane revealed that for acyl sulfates with less than about eight carbons there was a significant decrease in solubility and two phases developed. Upon addition of SO_3 the acyl sulfates would precipitate from solution as a heavy oil. The lower the molecular weight of the carboxylic acid, the more viscous and intractable the oil. It was difficult to obtain quantitative data from these insoluble acyl sulfates because of the problems of transferring the viscous oily precipitate. As the molecular weight of the acid increased, the performance improved and began to approach that of the totally soluble acyl sulfates.

Under some circumstances where SO_3 might be inconvenient to work with or to store, chlorosulfonic acid can be substituted for SO_3. Chlorosulfonic acid is a commodity chemical and does not require the storage facilities associated with liquid SO_3. However, hydrogen chloride is a byproduct from the reaction of chlorosulfonic acid with a carboxylic acid (eq 6). The performance of acyl sulfates generated from C_2 to C_{12} carboxylic acids by prior reactions with SO_3 or chlorosulfonic acid is shown in Table IV. The reagent prepared with octanoic acid was soluble in cyclohexane when sulfur trioxide was utilized but cloudy with chlorosulfonic acid. Perhaps the presence of HCl is sufficient to induce phase separation when there is a borderline solubility.

$$RCOOH + ClSO_3H \rightarrow RCOOSO_3H + HCl \quad (6)$$

The trend to improved performance with increasing size of the carboxylic acid is apparent in this table. It is reasonable to anticipate that the concentration of acyl sulfate in solution would increase as the increasing size of the

Table IV
Acyl Sulfate Efficiency as a Function of Carboxylic Acid Chain Length[a]

organic acid	product composition (mequiv/100 g) SO_3[b] titration	SO_3[b] S microanal.	$ClSO_3H$[b,c] titration	$ClSO_3H$[b,c] S microanal.	reagent solubility (cyclohexane, 20 °C)
acetic acid (C_2)		4.52	4.11	5.30	2 phases[d]
propionic acid (C_3)	12.23	12.16	5.01	5.30	2 phases
butyric acid (C_4)	16.44	15.38	8.71	8.11	2 phases
valeric acid (C_5)	19.27	20.90	21.20	20.90	2 phases
hexanoic acid (C_6)	20.56	19.96	16.09	15.91	2 phases
cyclohexanecarboxylic acid (C_7)	13.24	13.41	4.98	5.30	2 phases
octanoic acid (C_8)	24.02	24.49			homogeneous
			18.35	18.11	cloudy
dodecanoic acid (lauric acid) (C_{12})	25.80	25.90	27.39	28.38	homogeneous

[a] Polystyrene sulfonation at 50 °C; 100 g of polystyrene/500 mL of cyclohexane. [b] 40 mequiv premixed with 64 mequiv of carboxylic acid in 100 mL of cyclohexane at 25 °C. [c] In situ $ClSO_3H$ gives gelled polymer with low acid content. [d] Viscous insoluble acetyl sulfate difficult to transfer.

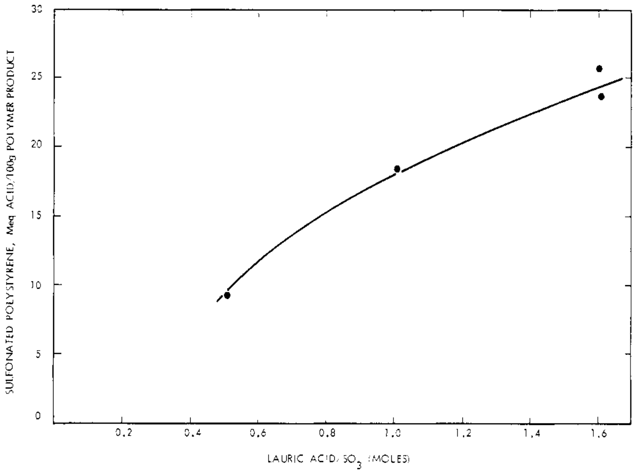

Figure 3. Effect of lauric acid/SO_3 ratio on polystyrene sulfonation (40 mequiv of SO_3).

hydrocarbon tail of the reagent improves its lipophilicity. As indicated earlier it was difficult to transfer the insoluble acyl sulfates but even this improved with molecular weight and the larger insoluble acyl sulfates could be dispersed in cyclohexane more readily. The convenience of handling the soluble acyl sulfates and the consistency of performance and uniformity of the product made them the reagents of choice.

The reagents described in this work were generally prepared by utilizing an excess of carboxylic acid over SO_3 or $ClSO_3H$. A convenient but arbitrary ratio of 1.6:1 acid to SO_3 was utilized to prepare the reagent in cyclohexane solution. Some reagents that are complexes of SO_3 such as sulfur trioxide–triethyl phosphate can utilize 2 mol or more of SO_3 to phosphate and gain in reactivity by doing so. Similarly, we wished to evaluate the utility of higher SO_3 complexes with our long-chain acids to see if these continued to show good solubility and enhanced reactivity. To the contrary (Figure 3) we observed decreased reactivity as the SO_3 to acid ratio was increased (acid to SO_3 decreased). Since higher ratios of SO_3 to acid should complex SO_3 more loosely and should be more reactive, we must presume that the lowered reactivity is the result of the lower solubility. Indeed, the separation of $2SO_3 \cdot C_{11}H_{23}COOH$ complex from cyclohexane is visible.

Acid Chlorides. The use of acid chlorides permits the in situ formation of acyl sulfates by reaction 7 with sulfuric

$$RCOCl + H_2SO_4 \rightarrow RCOOSO_3H + HCl \qquad (7)$$

acid. Here, as in the chlorosulfonic acid reaction with a carboxylic acid (reaction 6), HCl is a byproduct; however,

Table V
Polystyrene Sulfonation in Cyclohexane Using Acyl Chloride-H_2SO_4 Reagent[a]

acid chloride	mode	mequiv of sulfonation/100 g of polymer titration	S microanal.
acetyl chloride	in situ	12.27	12.48
acetyl chloride	premix[b]	9.79	9.36
propionyl chloride	in situ	23.73	24.64
butyryl chloride	in situ	20.23	20.90
hexanoyl chloride	in situ	25.60	26.51
octanoyl chloride	in situ	26.08	26.82
decanoyl chloride	in situ	29.46	30.88
lauroyl chloride	premix[c]	26.08	25.89

[a] 40 mequiv of H_2SO_4, 64 mequiv of acid chloride/100 g of polystyrene in cyclohexane at 50 °C; reaction time, 1 h. [b] Two phases; viscous reagent separates from cyclohexane. [c] Homogeneous solution in cyclohexane.

the latter reaction cannot be conducted in situ. Since acid chlorides are broadly available directly from the corresponding acid by reaction with a variety of chlorinating reagents (thionyl chloride, phosphorus chlorides, etc.) a range of acyl sulfates can be generated in situ and used as sulfonating reagents. The method is extremely effective. The solubility difference between the C_2 and C_3 reagent is significant and propionyl chloride gives twice the sulfonating efficiency of acetyl chloride (Table V).

The acid chlorides are more suitable for use as laboratory reagents. The expense of these reagents and the formation of HCl, which can be an undesirable byproduct, limits the commercial utility of this method.

Anhydrides. Acid anhydrides are not generally available because there are no convenient routes to produce them from the corresponding acids. Acetic anhydride is a longstanding exception since it can be produced by a specific route. Ketene, which is generated by pyrolysis of acetone, can be reacted with acetic acid to produce acetic anhydride (eq 8). Acetic anhydride is cheap and widely

$$CH_2{=}C{=}O + CH_3COOH \rightarrow (CH_3CO)_2O \qquad (8)$$

used in industry. More recently, propionic anhydride has become available as a commodity reagent manufactured by Eastman and Union Carbide. The substantial difference in performance between acetyl chloride and propionyl chloride prompted us to examine propionic anhydride to determine whether the unsatisfactory performance of acetic anhydride could be improved by so small an increase in molecular weight. Higher acid anhydrides, which are

Table VI
Polystyrene Sulfonation in Cyclohexane Using Acid Anhydride-H_2SO_4 Reagent[a]

		meqiv of sulfonation/100 g of polymer	
anhydride	mode	titration	S microanal.
acetic anhydride	in situ	6.92	6.86
propionic anhydride	in situ	21.31	21.83
butyric anhydride	in situ	24.14	24.95
stearic anhydride[b]	in situ	25.36	26.51

[a] 37.5 mequiv of H_2SO_4, 60 mequiv of anhydride/100 g of polystyrene in 500 mL of cyclohexane; reaction time, 1 h. [b] 40 mequiv of H_2SO_4, 50 mequiv of stearic anhydride.

available only from specialty chemical supply houses, were also examined to determine the extent of the trend (Table VI).

The results of the sulfonation of polystyrene in cyclohexane using propionic anhydride and H_2SO_4 to generate the acyl sulfate reagent in situ were most encouraging. The substantial improvement over acetic anhydride indicated that although the C_3 acyl sulfate has limited solubility in cyclohexane, the increased solubility makes a very significant difference in performance. Butyric anhydride showed slightly better performance, and then there was no significant difference from increasing the size of the acyl sulfate from C_4 to C_{18}. Although propionyl sulfate does not provide homogeneous sulfonations, its performance appears to be acceptable, especially when it is generated in situ from the anhydride, and there are no problems in handling and transferring the viscous reagent. The propionic acid byproduct should be innocuous. It is water soluble like acetic acid and easily removed from the polymers during precipitation or steam stripping. Propionic acid is a food additive used to preserve grain, so there should be no environmental objections to a process that generates this byproduct.

Neutralization. Neutralization of sulfonated polystyrenes described in this report have been carried out in a fashion similar to the neutralization of sulfonated EPDM polymers. A solution of excess metal acetate dissolved in 95:5 methanol–water is blended into the polymer cement, and the polymer is recovered by precipitation from a nonsolvent (isopropyl alcohol) or steam stripping. The polymer solution becomes a little more viscous upon neutralization but remains quite tractable. Neutralization with sodium methoxide in methanol in a quantity stoichiometric with sulfonate gives a similar result.

If excess sodium methoxide is utilized so that the carboxylic acid is also neutralized, the cement turns into an intractable viscous mass. Our understanding is that carboxylic acid is a vital cosolvent for the sulfonated polymer. Metal acetate in excess will not neutralize the carboxylic acid present in the system while the methoxide will. Addition of acetic acid to the polymer mass, obtained by treatment with excess methanolic sodium methoxide, restores a great deal of its original fluidity. It would appear that carboxylic acids are capable of solvating the sulfonates more effectively than the alcohol which is present in substantial quantity.

Other Homogeneous Reagents. In preliminary experiments with complexes of $2SO_3{\cdot}OP(OR)_3$ we observed that triethyl phosphate and tributyl phosphate complexes separated into two phases from cyclohexane solution, while tris(2-ethylhexyl) phosphate gave a homogeneous solution. The latter compound sulfonated the polystyrene efficiently while the triethyl phosphate complex did not. The data in Table VII compare the two. Note that only half of the SO_3 in the 2:1 complex is available for aromatic sulfonation.

Table VII
Sulfonation of Polystyrene in Cyclohexane Using Phosphate Ester-Sulfur Trioxide Complexes[a]

		meqiv of sulfonation/100 g of polymer	
phosphate ester	mode	titration	S microanal.
triethyl phosphate	premix	9.60	11.85
tris(2-ethylhexyl) phosphate	premix	21.20	22.45

[a] 40 mequiv of phosphate, 80 mequiv of SO_3/100 g of polystyrene. [b] 100 g of polystyrene in 500 mL of cyclohexane, 50 °C; reaction time, 1 h.

This reagent should prove useful in circumstances where carboxylic acid by-products are objectionable.

Summary and Conclusions

Earlier studies with olefin copolymers suggested that ineffective sulfonation with less reactive types of copolymers was due to the very low solubility of acetyl sulfate in the hydrocarbon solvent. Aromatic groups are substantially less reactive than olefins, so it seemed reasonable that past difficulties which were encountered in sulfonating polystyrene in hydrocarbon solvents were also due to the low solubility of acetyl sulfate.

We have now demonstrated that higher molecular weight (C_8) carboxylic acids can be utilized to produce hydrocarbon-soluble acyl sulfates by reaction with sulfur trioxide or chlorosulfonic acid. These preformed soluble acyl sulfates are very effective sulfonating reagents for polystyrene.

The use of higher molecular weight acid chlorides or anhydrides in situ with H_2SO_4 has also been shown to be effective at sulfonating polystyrene in cyclohexane solution. Propionic anhydride is substantially more effective than acetic anhydride. Since it is also a commodity chemical, it is the reagent of choice for heterogeneous in situ sulfonation of polystyrene in a hydrocarbon solvent.

Homogeneous sulfonations require carboxylic acids of at least eight carbons to preform a soluble acyl sulfate in hydrocarbon solution. Mixtures of saturated fatty acids in the detergent range may also be used to produce the sulfonating reagents and may be suitable dispersants for the direct production of a sulfopolystrene latex.

Some of the differences between the various reagents are more difficult to explain. In general, the in situ processes were more effective than the premix. Thus acid chloride and anhydride generated acyl sulfate, which could be formed directly in situ, was observed to be more efficient than the corresponding carboxylic acid/SO_3 reagents, which could only be utilized as a premix. The sulfonation of carboxylic acids to produce α-sulfocarboxylic acids is a well-known process, and it is not unreasonable that this side reaction could consume some of the reagent. Such a process would be more serious in the absence of the competing polystyrene polymer and might account for some of the differences.

A complex of sulfur trioxide with a high molecular weight phosphate ester has also been shown to produce a soluble sulfonating reagent superior in performance to acetyl sulfate. Soluble reagents that make chemically inert byproducts are desirable for some olefin copolymer reactions, and this will be explored further.

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References and Notes

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Preparation of (*p*-Vinylbenzyl)polystyrene Macromer

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ABSTRACT: In order to prepare a polystyrene macromer composed of only hydrocarbon, (*p*-vinylbenzyl)polystyrene macromer, the direct coupling reaction of polystyryllithium with an excess of *p*-vinylbenzyl chloride was carried out under various reaction conditions. The effect of solvent on the reaction was pronounced. When a solution of PSt-Li in a mixed solvent of benzene and THF (THF, ca. 20 vol %) was added dropwise to a solution of *p*-vinylbenzyl chloride in THF at 0 °C, the yield of the macromer was approximately 100% whereas when a smaller amount of THF was present in a polystyryllithium solution, the dimeric-terminated polystyryllithium formed to some extent as a byproduct. The characterization of the macromer obtained showed it to have one *p*-vinylbenzyl group per (*p*-vinylbenzyl)polystyrene molecule and an M_w/M_n of 1.0$_5$.

Introduction

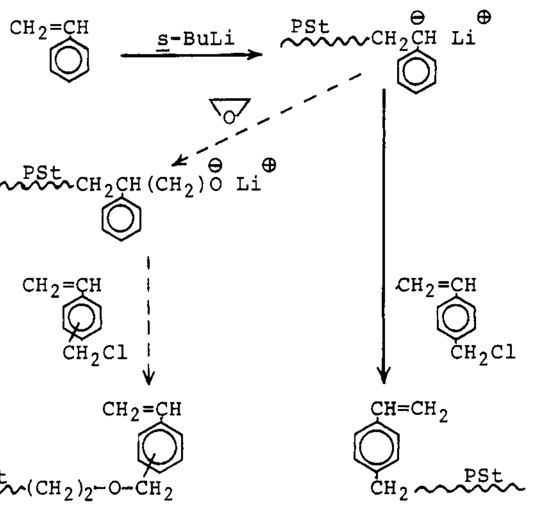
Since 1974, when Milkovich and Chiang[1] demonstrated the syntheses and applications of a variety of macromolecular monomers, which they called macromers, many reports have been published concerning the synthesis and/or application of this chemistry. Their concept has become a subject of growing importance.

Two methods have been used so far for the synthesis of polystyrene macromers. Milkovich and Chiang[1] prepared various vinyl types of polystyrene macromers by means of living polystyrene. On the other hand, recently Yamashita et al.[2] obtained polystyrene having a methacrylic group at a chain end by using the chain-transfer reaction in the radical polymerization of styrene.

In Milkovich's method for the synthesis of the polystyrene macromer, the living end of polystyrene prepared by anionic polymerization was first converted to an alcoholate end by reaction with ethylene oxide and then the intermediate was reacted with vinylbenzyl chloride, in order to exclude the reaction of the vinyl group of vinylbenzyl chloride with an original polystyryl living end. Therefore, the polystyrene macromer obtained by this method has an ether linkage between the vinylbenzyl and polystyrylethyl groups.

In the present study we prepared (*p*-vinylbenzyl)polystyrene containing no ether linkage by the direct reaction of living polystyrene with *p*-vinylbenzyl chloride. That is, polystyryllithium prepared by the polymerization of styrene with *sec*-butyllithium was reacted with an excess of *p*-vinylbenzyl chloride, thus skipping the reaction with ethylene oxide that Milkovich employed. The whole reaction is shown in Scheme I. Although it was considered that carbanions of the living polymer could react with both the double bond and the chloromethyl group of *p*-vinylbenzyl chloride, a model reaction[3] of *sec*-butyllithium with *p*-vinylbenzyl chloride suggested that the S_N reaction of carbanions with chloromethyl groups was much faster than the addition reaction of carbanions to the vinyl groups. The present paper describes that in this direct reaction of polystyryllithium with *p*-vinylbenzyl chloride, a polystyryl anion exclusively attacks the chloromethyl group and leaves the vinyl group of *p*-vinylbenzyl chloride unreacted, thus giving the polystyrene macromer quantitatively. The macromer thus obtained is composed of only hydrocarbon and is named as (*p*-vinylbenzyl)polystyrene. This is in contrast to the polystyrene macromer prepared by Milkovich, which would be termed as vinylbenzyl polystyrylethyl ether.

Scheme I



VB-PSt

Experimental Section

Materials. Polystyryllithium (PSt-Li) was prepared by polymerization of styrene with *sec*-butyllithium in benzene or THF. *p*-Vinylbenzyl chloride (*p*-VBC) was synthesized according to one[4] of the known methods. *p*-VBC was stirred with calcium hydride for 30 h and distilled over the drying agent in a high-vacuum system. Reagent grade *p*-methylstyrene was rectified just before its use. Benzene and tetrahydrofuran (THF) used as solvents of PSt-Li and *p*-VBC were purified by the usual methods and distilled in the presence of the sodium–benzophenone complex under high vacuum.

Coupling Reaction. The coupling reaction was performed by the following methods using three types of apparatus as shown in Figure 1. Method A: With apparatus A, a solution of PSt-Li in benzene (at ambient temperature) was added dropwise to a

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