decreases the viscosity of the solution. Further increase of alcohol concentration brings about a much smaller change in viscosity until at around the 4.3% level the viscosity becomes close to that of PSAC in toluene. The latter does not exhibit any discernible change in viscosity when alcohol is added to its solution in toluene (curve 6, Figure 3). The effect of temperature on viscosity of PSS solutions at various alcohol levels is different. Thus at the 1% level viscosity increases with an increase in temperature while at the others (2.5–4.3%) it decreases with temperature. Similar observations from studies using the sulfonated ionomers have been interpreted on the basis of an exothermic solvation equilibrium involving alcohols and the salt groups.[21-23] At the 1% alcohol level solvation is incomplete and increasing the temperature desolvates some of the solvated species and increases the viscosity of the solution while at higher alcohol concentrations solvation is complete and sufficient excess alcohol is present so that increasing the temperature over a 30 °C span fails to desolvate the polymers and viscosity decreases with temperature as is usually expected for the variation of viscosity with temperature.

Finally, we would like to point out that previously persulfate initiated emulsion polystyrene was reported to have low sulfate functionality ($f \simeq 0.2$) as measured by the dye extraction method of analysis[9] According to the same analytical method the present polymers prepared in a different way analyzed to have a sulfate functionality of 1.8 ± 0.1. The reason for the difference in sulfate functionality between conventional emulsion polystyrene and polystyrene as prepared here is being looked into.

Acknowledgment. Thanks are due to Dr. Suhas C. Guhaniyogi for the GPC analysis of the samples done at the University of Akron, Akron, OH. We also thank the referees for many helpful suggestions.

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Introduction of Nitrogen Functionality on Hydrogenated Butadiene/Styrene Copolymers

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Polymers containing functional groups are of interest because these groups can be sites for subsequent reactions, e.g., graft polymerization or for further modification. One method of preparing functional group containing polymers is by polymerization or copolymerization of functional monomers.[1,2] Another method is by chemical modification of a polymer. Platé, in a review,[3] discussed chemical modification of polymers and reactivity of functional groups on macromolecules, and more recently, 1982, Schulz, Turner, and Golub[4] extensively reviewed recent advances in the chemical modification of unsaturated polymers.

Butadiene homopolymer and butadiene/styrene copolymers contain olefin unsaturations that are active sites for chemical modification. Ethylene/propylene rubber (EP) contains no unsaturation and must be cured (cross-linked) by peroxides, but ethylene/propylene/diene rubber (EPDM) can be cured by sulfur because of unsaturation introduced by the diene termonomer.[5] Halasa[6,7] prepared anionic graft polymers by polylithiating polymer backbones with *n*-BuLi/*N,N,N',N'*-tetramethylethylenediamine (TMEDA) complex. Complexation with TMEDA dramatically increased the reactivity of *n*-BuLi.[8] EPDM (ethylene/propylene/1,4-hexadiene terpolymer) was polylithiated and reacted subsequently with CO_2 to introduce carboxy functionality.[7] Waldbillig[9] prepared graft polymers of EPDM by the reaction of (dialkylamino)alkyl methacrylates with the polylithiated (*n*-BuLi/TMEDA) polymer.

Hydrogenated butadiene/styrene copolymer does not contain olefin unsaturation. The aromatic groups of the polystyrene must provide the active sites for functional modification. Cationic reactions such as chlorination and sulfonation are difficult to control and can result in gelled, highly cross-linked polymers. There are numerous examples of utilization of the aromatic activity of styrene for polylithiation. For example, divinylbenzene–styrene polymer was brominated smoothly in the presence of Tl(II) salt catalyst and the product easily lithiated by treatment with excess *n*-butyllithium.[10] The polymer also was directly lithiated with *n*-butyllithium and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) complex. The lithiated residues were converted subsequently to polymers containing –CO_2H, –SH, sulfide, –$B(OH)_2$, amide, silylchloride, phosphine, bromide, alcohol, and trityl groups, respectively, for use in polymer associated synthesis. Polystyrene itself has been polylithiated by n-BuLi/TMEDA complex and analytical procedures developed to determine the extent of polylithiation.[11,12]

The following study was undertaken to develop conditions for introducing nitrogen functionality on hydrogenated butadiene/styrene copolymer. We chose the approach utilizing polylithiation and subsequent reaction with a dimethylamino-containing carbonyl compound. The product, subsequent to hydrolysis, contained both dimethylamino and hydroxyl functionality.

$$\mathrm{Bd(H)/Styr} + x\mathrm{BuLi/TMEDA} \rightarrow \mathrm{Bd(H)/Styr(Li)}_x + \mathrm{BuH}\uparrow \xrightarrow[\mathrm{H}^+]{\mathrm{(CH_3)_2NR\text{-}C(R')O}} \mathrm{Bd(H)/Styr\text{-}(C(R')OHRN(CH_3)_2)}_x \quad (1)$$

p-(Dimethylamino)benzaldehyde was used because it is relatively free of reactive sites for competing and secondary reactions; e.g., labile hydrogens on the carbon adjacent to a carbonyl or ester group for elimination and subsequent coupling, etc. Zelinski, Hsieh, and Strobel[13] combined p-(dimethylamino)benzaldehyde and lithium telechelic polybutadiene to prepare telechelic, terminally functional polymers.

Experimental Section

Polymer Syntheses. Phillips rubber grade butadiene, Phillips polymerization grade cyclohexane (85%), and Dow polymerization grade styrene were purified by passage over activated alumina (Kaiser KA201). Tetrahydrofuran (Matheson Coleman and Bell) and *N,N,N',N'*-tetramethylethylenediamine were dried and stored, after a nitrogen sparge, over activated alumina. Butyllithium, a heptane solution from Foote Mineral Corporation, was diluted with cyclohexane before use. Nickel 2-methylheptanoate was obtained from Witco Chemical Co. Triethylaluminum in heptane solution was obtained from Texas Alkyls. The nickel and aluminum compounds were diluted with cyclohexane for ease of handling.

Mixtures (13.1 wt %) of butadiene and styrene in cyclohexane containing 0.23 wt % tetrahydrofuran (as randomizer and 1,2-polymerization promoter) were polymerized with n-butyllithium initiator. Sequential polymerization of styrene and butadiene was employed for preparation of block copolymers. Either typical bottle polymerization techniques were employed[14] or polymerizations were carried out in a half-gallon, glass Chemco reactor. Reactions were blanketed with a nitrogen atmosphere.

Polymer solutions, quenched by a small amount of ethanol, were hydrogenated in a half-gallon, glass Chemco reactor maintained at 345 kPa (50 psig) hydrogen pressure. The hydrogenation catalyst (0.29 g of Ni/100 g of polymer) was added as a preformed, 2/1 molar ratio mixture of triethylaluminum/nickel 2-methylheptanoate in dry cyclohexane (0.3 M Ni). Nickel hydrogenation catalyst residues were oxidized with air, treated with aqueous ammonium phosphate, and removed by filtration as insoluble metal phosphates.

Total styrene content of the polymer was determined from ultraviolet absorption at 262 nm. Block styrene content of the unhydrogenated polymer was determined by oxidative degradation based on the method of Kolthoff, Lee, and Carr.[15] Percent of total unsaturation as trans and vinyl, 1,2-addition, were determined by infrared absorption spectroscopy at 966 cm^{-1} (10.35 μm) and 909 cm^{-1} (11.0 μm), respectively. Normalized unsaturations are corrected for the amount of styrene present in the polymer; i.e., they are the percentages of polybutadiene unsaturation present in the cis/trans/vinyl configuration. Molecular weights were determined by gel permeation chromatography using Waters μ–Styragel columns with THF as the carrier solvent. Calibration and calculations were by the method of Kraus and Stacy.[16]

Polylithiation. Polymer was dissolved in cyclohexane, 0.91 wt %, and sparged with nitrogen to remove dissolved oxygen. n-Butyllithium (n-BuLi) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were added by hypodermic syringe as cyclohexane solutions. Reactions were carried out either in beverage bottles closed with self-sealing gaskets and crown caps and agitated in a constant temperature bath, or in a glass, stirred Chemco reactor. No differences were noted between polylithiation reactions in either the stirred reactor or beverage bottles. Agitation was poor in either case because of the high solution viscosity of the lithiated polymer.

Functionalization. Polylithiated polymer in cyclohexane at 50 °C was reacted with 10 mol % excess of p-(dimethylamino)benzaldehyde (purified by recrystallization from cyclohexane). A mechanical stirrer was necessary to stir the reaction mixture, which was blanketed with nitrogen. The functionalized polymer (eq 1) was quenched by ethanol and isolated by coagulation with a nonsolvent (2-propanol). The polymer was dissolved in cyclohexane and recoagulated a total of 3 times to remove unreacted p-(dimethylamino)benzaldehyde and TMEDA. Nitrogen content of the dried polymer remained constant after three coagulations, indicating complete removal of nitrogen contaminants. Nitrogen content of dried polymer was determined with an Antek 707 chemiluminescent nitrogen analyzer from Antek Instruments, Inc., Houston, TX. The method of analysis involves complete oxidative pyrolysis of the sample, conversion of chemically bound nitrogen to nitric oxide, which is then reacted with ozone to produce metastable nitrogen dioxide. The nitrogen dioxide chemiluminesces upon relaxation. This light emission is proportional to the amount of nitrogen in the sample and is detected by a photomultiplier tube, and the signal is integrated for digital display. This procedure was described by R. E. Parks, Antek Instruments, Inc., at the 1976 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, and in the instrument manual. The results can be considered accurate to ±10% of the reported value for low nitrogen concentrations.

Results and Discussion

Polylithiation. Polylithiation was done by the reaction of hydrogenated butadiene/styrene copolymers in cyclohexane with a 1:1 molar ratio complex of n-butyllithium (n-BuLi) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA). A typical polymer before modification contained 56.2 mol % butadiene (40 wt %) and 43.8 mol % styrene (60 wt %). Tetrahydrofuran (1.54 g/100 g of monomer) was used in the polymerization to partially randomize styrene addition to the growing polymer lithium. The THF also increased the vinyl content of the polymer from about 8% to 27%. It is difficult to obtain complete randomization with such a high styrene content. As the polymer forms, butadiene is incorporated faster than styrene, which changes the ratio of remaining butadiene and styrene monomer. At about 82% conversion, butadiene monomer is depleted and the remaining 18 parts of styrene polymerize to form a terminal end block of polystyrene. Within the random portion of the polymer, styrene content becomes progressively greater from the beginning of the chain to the polystyrene end block. The product is commonly referred to as a tapered block or random-block copolymer. Block styrene determined by oxidative degradation before hydrogenation was 18 wt %. Normalized vinyl content, 1,2-addition, before hydrogenation was 27%. Vinyl unsaturation after hydrogenation was undetectable by infrared absorption. Number average molecular weight as determined by gel permeation chromatography of a typical polymer was 65 000.

Polylithiation was followed by butane evolution, Figure 1, and by solution viscosity increase, Figure 2. The gas phase above the polylithiation reaction was sampled and analyzed by GC for n-butane using *iso*-butane as an internal standard. Reaction was rapid at 70 °C for the first 45 min and accounted for about 76% of the n-butyllithium added. The rate of reaction then decreased and the total amount of n-butane detected after 90 min accounted for 78.4% of the n-butyllithium. While some n-butane could also arise from decomposition of n-butyllithium/TMEDA complex, n-butane evolution did stop in a short time, and

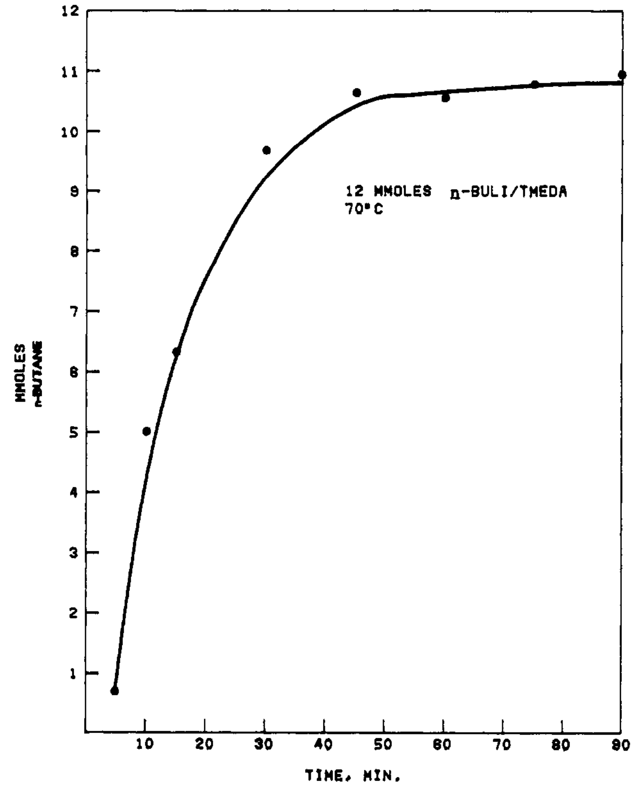

Figure 1. Butane evolution on polylithiation of hydrogenated butadiene styrene copolymer.

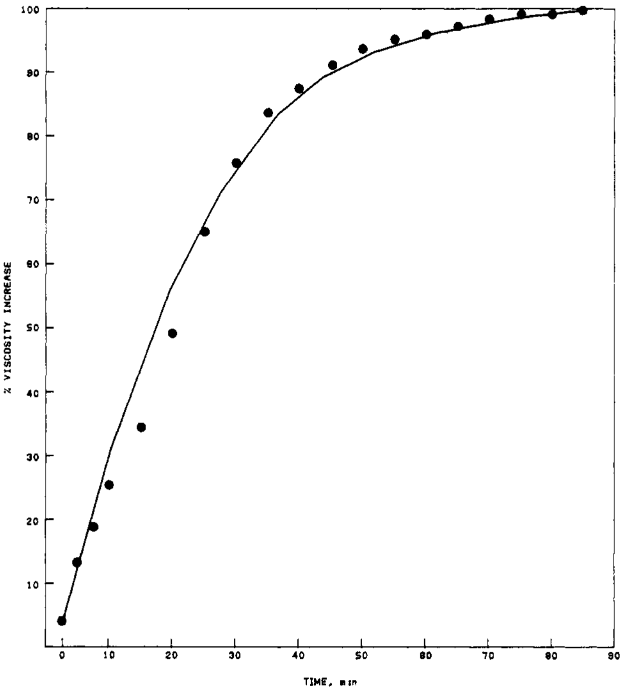

Figure 2. Viscosity increase of polylithiated hydrogenated butadiene/styrene copolymer.

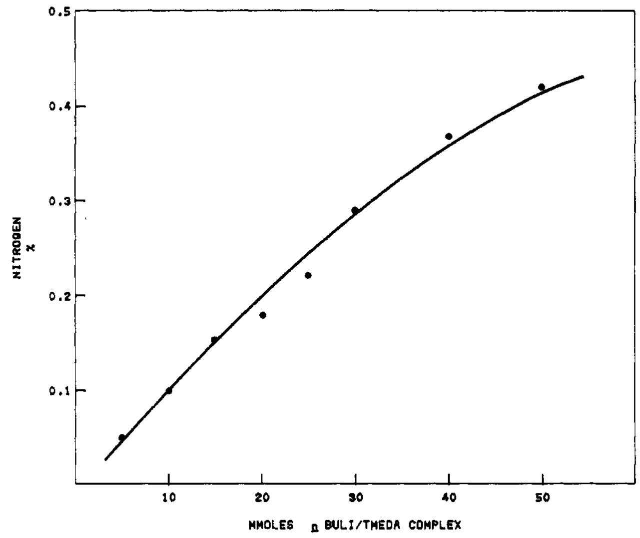

Figure 3. Effect of *n*-buli amount on nitrogen incorporation on hydrogenated butadiene/styrene copolymer.

Table I
Effect of *n*-BuLi Amount on Nitrogen Incorporation in Hydrogenated Butadiene/Styrene Copolymer

n-BuLi/TMEDA,[a] mmol	nitrogen content, wt % theoretical[b]	nitrogen content, wt % found	reaction efficiency,[c] %
5	0.07	0.05	71
10	0.14	0.10	71
15	0.21	0.15	71
20	0.28	0.18	64
25	0.35	0.22	63
30	0.42	0.29	69
40	0.56	0.37	66
50	0.70	0.42	60

[a] Millimoles per hundred grams of polymer treated. [b] Assuming one nitrogen per lithiation site (using 100% lithiation). [c] (Nitrogen found/theoretical nitrogen) × 100.

n-butane evolution can be used to determine when metalation, lithiation, is complete. Only a small amount of polymer degradation could be detected by gel permeation chromatography of the functionalized polymer.

The increase in polymer solution viscosity as polylithiation proceeded was followed utilizing a Dynatrol viscosity system. The procedure used was developed by Hsieh and Kitchen[17] for continuously measuring changes in polymer solution viscosities as the polymerlithium varied in degree of association or degree of polymerization. Polylithiation was assumed to be complete when the maximum viscosity increase was obtained. Polylithiation caused an increase in lithium association, a recognized phenomenon of organolithium compounds.[18] Use of tetrahydrofuran as a reaction solvent would have avoided some of the cement viscosity problems through decreased polymerlithium association but would have added the complication of organolithium/ether decomposition reactions. The maximum viscosity increase of the polylithiated polymer solution occurred between 70 and 80 min. Subsequent polylithiations discussed in this paper were done at 70 °C for 90 min.

The polymer solution became quite viscous between 30 and 45 min of polylithiation, and little agitation took place after 45 min in a glass, stirred Chemco reactor. Viscosity of the untreated polymer solution at 70 °C was measured[19] as 14.65 cP, and viscosity of a polylithiated (12 mmol of *n*-BuLi/TMEDA) solution was 3800 ± 40 cP (measured at 70 °C with a Cannon–Ubbelohde viscometer in a nitrogen atmosphere).

Effect of *n*-BuLi/TMEDA Level on Nitrogen Functionality. Hydrogenated 40/60 weight ratio butadiene/styrene random-block copolymers (constant monomer ratio) were polylithiated with variable amounts of 1:1 molar ratio *n*-BuLi/TMEDA complex, and the polylithiated polymer was allowed to react with *p*-(dimethylamino)benzaldehyde. The hydrolyzed, purified, and dried polymers showed almost a linear relationship of nitrogen content and *n*-BuLi complex level used, Figure 3. Vis-

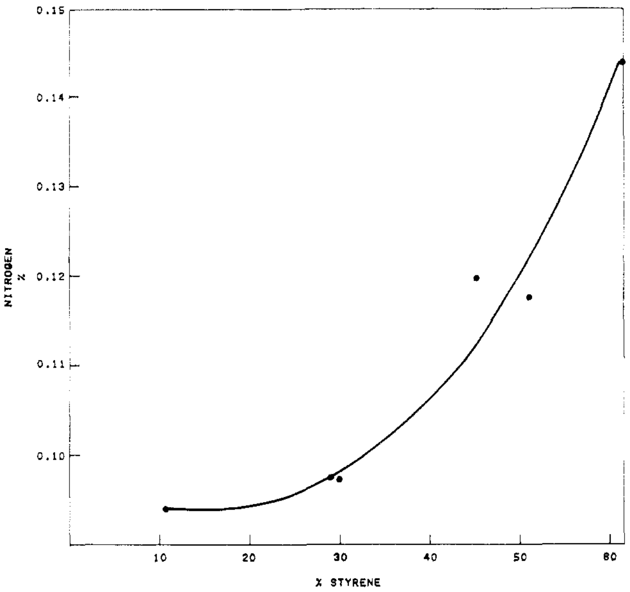

Figure 4. Effect of styrene content of copolymer on nitrogen incorporation.

Table II
Effect of Styrene Content of Copolymer on Nitrogen Functionality

butadiene/styrene weight ratio	nitrogen content, wt %		reaction efficiency,[b] %
	theoretical[a]	found	
40/60	0.196	0.14	71
50/50	0.196	0.12	61
60/40	0.196	0.12	61
70/30	0.196	0.07	36
80/20	0.196	0.08	41
90/10	0.196	0.04	20

[a] Based on 14 mmol of *n*-BuLi/TMEDA complex/100 g of polymer and 100% lithiation and reaction iwth *p*-(dimethylamino)benzaldehyde. [b] (Nitrogen found/theoretical nitrogen) × 100.

Table III
Nitrogen Functionality on Hydrogenated Butadiene-Styrene Block Copolymer

total styrene, wt %	block styrene,[a] wt %	nitrogen,[b] %
60	8.5 (random block)	0.10
60	58 (block)	0.14
40	30 (block)	0.10
20	15 (block)	0.09

[a] Determined by oxidative degradation before hydrogenation. [b] 14 mmol of *n*-BuLi/TMEDA complex and 15.4 mmol of *p*-(dimethylamino)benzaldehyde/100 g polymer were used.

cosity of the polylithiated polymer solution increased with increased *n*-BuLi/TMEDA concentration, which probably affected the extent of reaction at high levels. The amount of nitrogen found was less than theoretical, Table I, and reaction efficiency decreased with increasing *n*-BuLi/TMEDA level, probably also because of increased solution viscosity.

Effect of Styrene Content of Copolymers on Nitrogen Functionality. The amount of nitrogen functionality found in hydrogenated butadiene/styrene random-block copolymers polylithiated with a constant amount of *n*-BuLi/TMEDA complex (14 mmol) and subsequently treated with *p*-(dimethylamino)benzaldehyde decreased as the amount of styrene in the copolymer decreased, Figure 4. Nitrogen content as percent of the theoretical amount decreased from 71% to 20%, showing the importance of styrene content for polylithiation, Table II. These results are consistent with results of Evans et al.,[20] who showed that metalation of polystyrene is first order in polystyrene and first order in *n*-butyllithium. The curve of Figure 4 may not go through the origin because there may also be a small amount of metalation in the diene section of the polymer where some residual unsaturation remains.

There is much more styrene available for polylithiation than is accounted for by the nitrogen incorporation. (A referee has suggested the possibility of a Cannizaro reaction of the initially formed alkoxide with the benzaldehyde to generate benzophenone functionality. This could then react inter- or intramolecularly to give less than one nitrogen per metalation site.) A hydrogenated 40/60 butadiene/styrene copolymer with M_n of about 59000 containing 0.14% nitrogen contains about 340 monomer units of styrene but only about six functionalized styrene units.

Hydrogenated butadiene/styrene block copolymers also were polylithiated and derivatized with *p*-(dimethylamino)benzaldehyde. Table III shows results with hydrogenated butadiene/styrene block copolymers. Regardless of whether the styrene is random or block in the copolymer, it can be modified by polylithiation.

An attempt was made to determine the position of the dimethylamino group on a functionalized hydrogenated butadiene/styrene copolymer by proton NMR. A $(CH_3)_2N$ functional group could be detected by a weak resonance at 3.9 ppm, but weakness of the signal precluded the possibility of determining the position of substitution. Chalk[21] reported ring-substituted products on metalation of polystyrene with *n*-butyllithium/TMEDA. Even though the position of polylithiation, hence nitrogen functionality, on the hydrogenated butadiene/styrene molecule was not proved, there can be little doubt that styrene was a dominant factor and that it is important for extensive lithiation.

Registry No. (*n*-BuLi)·(TMEDA) (1:1), 88454-13-1.

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Hydration Effects in the ^{13}C CP/MAS NMR Spectra of Solid (1→3)-β-D-Glucans

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Several solid polysaccharides have been examined by ^{13}C CP/MAS NMR. It has been shown that the ^{13}C spectra of cellulose depend strongly on the source of natural cellulose I.[1,2] In addition, characteristic spectra are observed for the different polymorphic forms of cellulose.[3,4] It is clear that particular features of the ^{13}C spectra of these materials, such as peak multiplicities and line widths, reflect differences in the detailed structures of the various samples, although the precise interpretation of the observed differences is somewhat controversial. Recently, Saitô et al. have reported ^{13}C NMR studies of solid (1→3)-β-D-glucans from a variety of sources.[5] Variations in peak positions in the ^{13}C spectra of these materials were ascribed by these authors as due to conformational differences in the solids, related to the ability to form gels in aqueous media.

We have noted that the ^{13}C NMR spectra of these materials are quite sensitive to sample history. In particular, the widths of the ^{13}C resonances vary dramatically with the moisture content of the solids. Smaller variations are also observed in the chemical shifts. The present data indicate that sample history must be carefully considered in the interpretation of the ^{13}C spectra of these materials.

The ^{13}C CP/MAS spectra were obtained at 22.6 MHz, as previously described.[4] Spectra were recorded for purified curdlan and depigmented paramylon, using dry, as-received materials and in the presence of excess water. The curdlan sample was provided by the Takeda Chemical Co., Japan, and the paramylon sample, derived from *Euglena gracilis*, was a gift from Prof. Bruce Stone of La Trobe University, Australia. Figures 1 and 2 show the spectra obtained for each sample in the dry and hydrated forms.

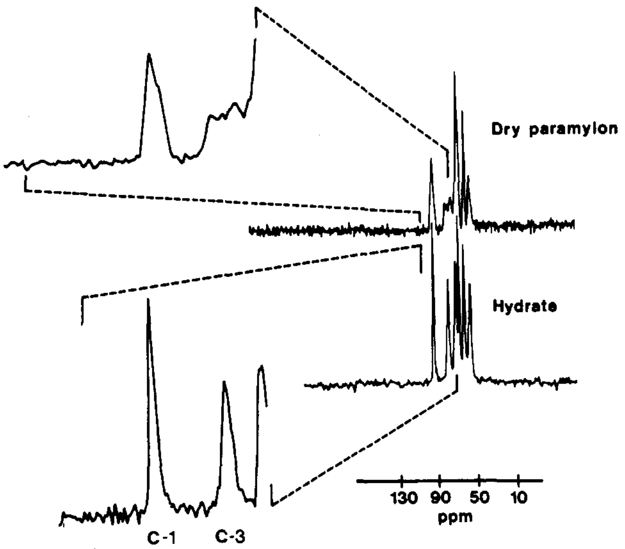

Figure 1. ^{13}C CP/MAS spectra of solid paramylon in the dry and hydrated forms.

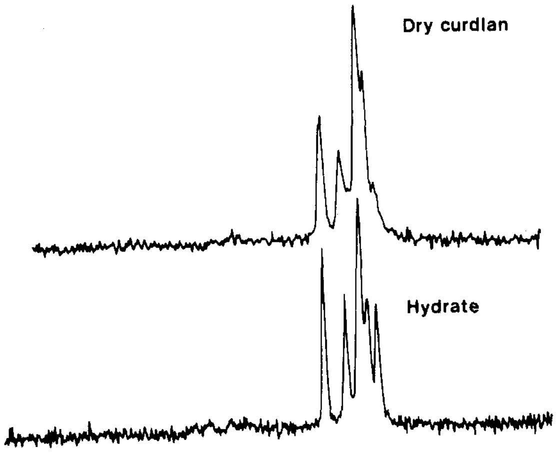

Figure 2. ^{13}C CP/MAS spectra of solid curdlan in the dry and hydrated forms.

In both cases, it is clearly seen that hydration of the solids results in a dramatic narrowing of the ^{13}C resonances. This effect is most pronounced for the C-1 and C-3 resonances of paramylon shown inset in Figure 1. In the dry material, these resonances both display fine structure similar to that noted by Saitô et al.[5] In the presence of excess water, these resonances in the paramylon spectrum are very sharp and show no indication of fine structure. Chemical shift differences are most pronounced in the C-3 region, where multiple resonances are found in the dry form while only a single line is apparent in the hydrated material. The spectral changes associated with hydration are similar, though less dramatic, for the curdlan samples. Saitô et al.[5] interpreted the fine structure of the C-3 resonance as being characteristic of native and alkaline regenerated forms of curdlan and interpreted it in terms of helical structures, but it is now clear that this fine structure is due to hydration effects.

It is difficult to assign the cause of the observed spectral changes in an unequivocal manner. Similar variations noted in ^{13}C spectra of celluloses have been attributed to differences in morphology[2,6] or crystallinity.[7] It is interesting to note that broader lines are observed in the spectra of both dry and hydrated curdlan samples than are found in the corresponding paramylon spectra. This may reflect a lower crystallinity for curdlan relative to paramylon. The curdlan may be expected to be less crystalline since its purification process involves solubilization and reprecipitation, whereas the paramylon is examined in its native, highly crystalline form. X-ray powder diffraction studies were carried out on the two polysaccharides, using both dry and hydrated samples. Figure 3 shows the diffraction traces obtained. For paramylon, both dry and hydrated samples exhibit high degrees of crystallinity, with the greater crystalline order found in the hydrate form. In contrast, neither curdlan sample shows sharp reflections characteristic of crystalline regions. Thus, while the differences in the ^{13}C line widths between the curdlan and paramylon may be related to crystallinity effects, the decrease in widths noted on hydration of both samples cannot be attributed solely to crystallinity changes.

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