hydrochloride salt was dried under reduced pressure (0.05 mm) over phosphorus pentoxide at 100°. The free amine obtained by the method of Vogel and Marvel[9] from the tetrahydrochloride salt was purified by sublimation at 150–160° (0.1 mm), mp 273–274° (lit.[9] mp 274–276°).

7H-Benzimidazo(2,1-*a*)benz(*de*)isoquinolin-7-one (V). This model compound was prepared as previously described.[9,17]

N-(2-Aminophenyl)naphthalimide (VI). This model compound was prepared as previously described.[9,17]

Polycondensation Using Free Tetraamine. To a 500-ml three-necked flask fitted with a trubore stirrer and nitrogen inlet and outlet was added 250 g of PPA. The PPA was deoxygenated by heating overnight at 110° with nitrogen bubbling through the stirred acid. Under a nitrogen atmosphere at 50° were added 1.38 g (0.01 mol) of TAB and 3.04 g (0.01 mol) of NTCA. The mixture was slowly heated (4°/min) to 180° and maintained at that temperature for 10 hr. The resulting viscous solution was poured out of the flask at 180° into a beaker and allowed to cool to room temperature. The polymer was precipitated in methanol, using a blender to facilitate mixing. The fibrous brown material was washed twice with 1-l. portions of anhydrous methanol and dried at 200° under reduced pressure (0.40 mm). Precipitation from 500 g of methanesulfonic acid and drying in the above manner gave 3.2 g (95%). An intrinsic viscosity of 5.00 dl/g in 100% methanesulfonic acid was determined.

Anal. Calcd for $C_{20}H_8N_4O_2$: C, 71, 86; H, 1.81; N, 16.76. Found: C, 70.08; H, 2.01; N, 16.08; residue, 0.9. Residue by emission spectra analysis contained mainly silicon and traces of various metals.

Polycondensation Using Tetraamino Tetrahydrochloride. Polymerizations using TAB·4HCl were carried out in a similar manner; however, the NTCA was not added until all the hydrogen chloride was thermally displaced from the tetraamine. This was accomplished by heating the tetraamino tetrahydrochloride in deoxygenated PPA overnight at 75–80°.

Polymer End Capping. To 100 g of deoxygenated PPA were added 0.500 g of polymer with intrinsic viscosity 5.00 dl/g and 2 g of *o*-phenylenediamine. The solution was slowly heated (4°/min) to 180° and 2 g of additional *o*-phenylenediamine was added. After 8 hr at 180°, the mixture was cooled to room temperature and precipitated into 2 l. of anhydrous methanol. The finely divided precipitated material was washed with methanol and dried under reduced pressure (0.40 mm).

Acknowledgment. This work was supported in part by Air Force Materials Laboratory Director's Discretionary Funds. The authors with to thank Dr. John F. Coleman, Captain, USAF, for isothermal aging data.

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(17) M. J. Okagaki, *J. Soc. Org. Chem. Jap.*, **13**, 80(1955); *Chem. Abstr.*, **51**, 27452 (1967).

Sulfonyl Carbamate Derivatives of Cellulose[1]

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ABSTRACT: *p*-Toluenesulfonyl isocyanate (*p*-TSI) reacts with cellulose to produce a *p*-toluenesulfonylcarbamate derivative. O-Alkyl N-*p*-toluenesulfonylcarbamates exhibit pK_a's comparable to carboxylic acids; this represents a new acidic ionogenic group for cellulosic ion exchange resins. Treatment of a slurry of cotton linters in pyridine with 4 mol of *p*-TSI/mol of cellulose effects solution within 2 hr at 80°. A degree of substitution of 2.0 is attained rapidly but reaction times of 18 hr or more are required to achieve quantitative substitution. The formation of a pyridine–*p*-TSI complex decreases the activity of *p*-TSI at reaction temperatures below 70°, but inert solvents such as chlorobenzene or dioxane fail to dissolve the cellulose derivative and no substitution occurs. Neither $ZnCl_2$ nor dibutyltin dilaurate was effective in catalyzing the process. Derivatives with residual hydroxyl groups could be cross-linked with bis(4-isocyanatophenyl) isocyanate, *p*-(isocyanatophenyl)sulfonyl isocyanate, or chlorosulfonyl isocyanate to form resins which swell but do not dissolve in 2% NaOH. The ion exchange capacity of these resins was found to be 2.9 mequiv/g.

Recent improvements in the synthesis techniques of sulfonyl isocyanates indicate that a new look at their application to the modification of polymeric materials could be beneficial. Ulrich and Sayigh[3] have developed a procedure by which aromatic sulfonyl isocyanates can be prepared by the direct phosgenation of the corresponding sulfonamides in the presence of catalytic amounts of butyl isocyanate. Sulfonyl isocyanates exhibit enhanced reactivity toward nucleophilic attack by alcohols, amines, phenols, thiols, and some aromatic compounds containing activated carbon–hydrogen bonds. In contrast to aryl isocyanates, sulfonyl isocyanates react quantitatively with phenols and sterically hindered alcohols to produce sulfonylcarbamate derivatives.[4] This suggests that they would be sufficiently reactive to disrupt the crystallinity of native cellulose. We have found that *p*-toluenesulfonyl isocyanate (*p*-TSI) reacts with untreated cellulose to pro-

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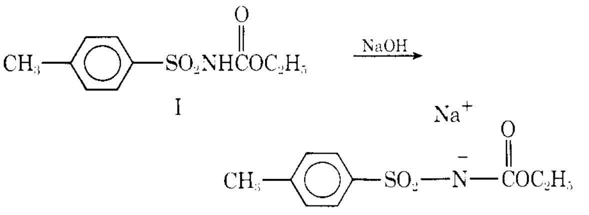
(2) (a) Department of Chemical Engineering; (b) Department of Chemistry; (c) to whom inquiries should be addressed.

(3) H. Ulrich and A. A. R. Sayigh, *Angew. Chem. Intern. Ed. Engl.*, **5**, 704 (1966).

(4) J. McFarland and J. B. Howard, *J. Org. Chem.*, **30**, 957 (1965).

duce derivatives with high degrees of substitution in the absence of catalyst.

In addition, the sulfonylcarbamates exhibit an acidity comparable to that of acetic acid. A brief communication by Taylor, Pluhar, and Rubin reports that the pK_a of O-ethyl N-*p*-toluenesulfonylcarbamate (I) in aqueous media is 3.7.[5] Although the acidity of sulfonamides is well known (Hinsberg test), the magnitude of acidity of the sulfonylcarbamates as well as the sulfonyl ureas was unexpected. Thus sulfonyl isocyanates present a unique opportunity to convert a basic or neutral functional group which contains an active hydrogen to a relatively strong acid using very mild and essentially neutral conditions.



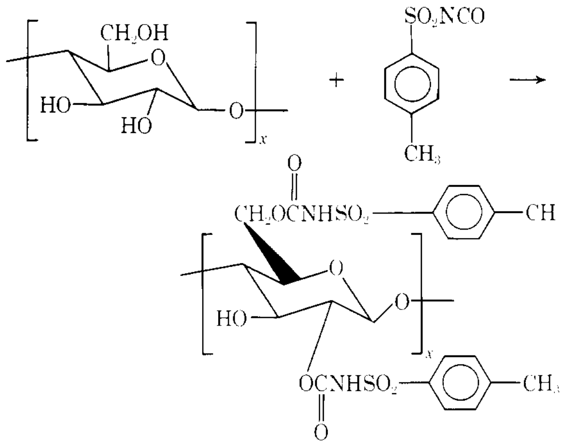
The reaction of aryl isocyanates with cellulose to produce aryl carbamate derivatives is well documented.[6] Hearon, *et al.*,[7] found that reaction times of 36 hr were required to get substantial reaction of phenyl isocyanate with cellulose. Ellzey and Mack[6b] conclude that the reaction medium used must be able to swell cellulose even if only slightly. Several catalysts for this reaction were studied by Volozhin, *et al.*;[6c] transition metal catalysts were found to be much more effective than tertiary amine catalysts. In fact, pyridine was found to be such an ineffective catalyst that transition metal catalysts were usually added when pyridine was used as the reaction medium. Further rate enhancement was observed when the catalyzed reaction was carried out in aprotic solvents such as dimethyl formamide or dimethyl sulfoxide. In none of the work listed above were pure cotton linters used as the substrate. Rather, either cellulose acetate, methylcellulose, pretreated cellulose, or regenerated cellulose was used.

The stability of carbamate linkages in the presence of acids has been demonstrated, but a slight degradation occurs under basic conditions.[8] However, Taylor, *et al.*, comment on the remarkable stability of the sulfonylcarbamate linkage to alkaline conditions. They also report the preparation of polymeric acids by the reaction of *p*-toluenesulfonyl isocyanate with polymeric alcohols including cellulose diacetate in benzene. We have observed that soluble polymeric substrates are not required providing that the derivative formed dissolves in the reaction medium.

All of these factors combine to indicate that sulfonylcarbamate derivatives of cellulose could be used as cation exchange resins. Cellulose has been used as a substrate for ionogenic groups for several years. The high surface area of the cellulose fiber, coupled with its hydrophilic character, makes cellulose an ideal substrate for the separation of polyelectrolytes such as proteins, nucleic acids, and other natural products.[9] Further advantages of cellulosic resins lie in their natural insolubility, which eliminates the problem of achieving uniform cross-linking, and the wide choice of physical forms available for different applications. The introduction of a substituent group with acidic properties represents one of the earliest and most successful methods for synthesizing cellulosic ion exchange resins. The most common cellulose cation exchange resin is carboxymethylcellulose (CMC), but the nature of the acidic group has been varied to include the half-ester of succinic acid or phthalic acid as well as strong acids such as phosphoric and sulfonic acid derivatives. A large portion of the initial work on these derivatives was reported by Guthrie and coworkers.[10] The specific application of these and other cellulosic ion exchange resins is the subject of a recent review which cites 500 references.[11] One can expect the intense interest in this field, particularly in biological applications, to continue unabated.

Discussion

Our initial approach to the utilization of sulfonyl isocyanates in polymer modification was directed toward the preparation of cellulose derivatives. Cellulose was selected as the polymer substrate because of its natural abundance and its potential as an ion exchange resin. Further, the relative inertness of untreated cellulose toward chemical modification is well established, so that reaction conditions which lead successfully to cellulose derivatives could probably be applied to all other types of polymeric alcohols. Therefore, emphasis was placed upon evaluating and optimizing the synthesis techniques for cellulosic sulfonylcarbamates (II) with varying degrees of substitution and investigating their properties.



II

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(5) L. D. Taylor, M. Pluhar, and L. E. Rubin, *Polym. Lett.*, **5**, 77 (1967).

(6) (a) E. Huseman and G. J. M. Muller, *Makromol. Chem.*, **91**, 212 (1966); (b) S. E. Ellzey, Jr., and C. H. Mack, *Textile Res. J.* **32**, 1023 (1962); (c) A. I. Volozhin, O. P. Kozmina, and S. N. Danilov, *Zh. Prikl. Khim.*, **37**, 1578, 2327 (1964); *Chem. Abstr.*, **62**, 5432*g* (1964).

(7) W. M. Hearon, G. D. Hiatt, and C. R. Fordyce, *J. Amer. Chem. Soc.*, **65**, 829 (1943).

(8) W. M. Hearon, G. D. Hiatt, and C. R. Fordyce, *ibid.*, **65**, 833 (1943).

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(9) E. A. Peterson and H. A. Sober, *J. Amer. Chem. Soc.*, **78**, 751 (1956); (b) H. A. Sober, F. J. Gutter, and M. M. Wyckoff and E. A. Peterson, *ibid.*, **78**, 756 (1956).

(10) C. L. Hoffpauir and J. D. Guthrie, *J. Biol. Chem.*, **178**, 207 (1949); (b) C. L. Hoffpauir and J. D. Guthrie, *Textile Res. J.*, **20**, 617 (1950); (c) J. D. Guthrie, *Ind. Eng. Chem.*, **44**, 2187 (1952).

(11) E. G. Davidova and V. V. Rachinskii, *Russ. Chem. Rev.* **34**, 104 (1965).

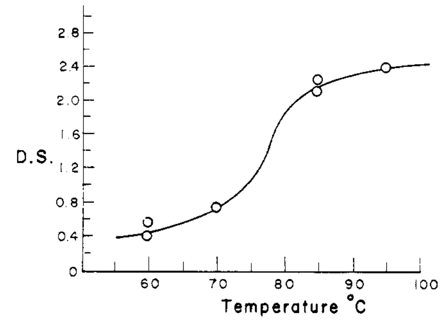

Figure 1. Degree of substitution attained at various temperatures using a 4:1 mole ratio of *p*-TSI–cellulose after 1 hr. The degree of substitution (D.S.) was determined from sulfur content.

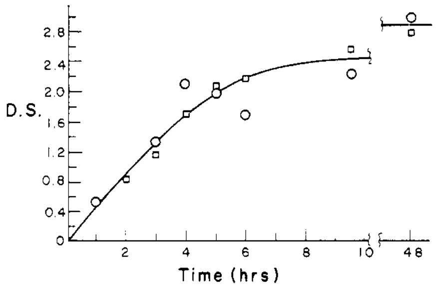

Figure 2. Degree of substitution attained at various reaction times using a 4:1 mole ratio of *p*-TSI-cellulose at 70°: ○, based upon sulfur content; □, based upon weight gain.

Reaction Conditions. Owing to the reactivity of sulfonyl isocyanates, the selection of the reaction media is limited. Polar aprotic solvents such as dimethyl formamide or dimethyl sulfoxide react with *p*-TSI to produce N,N-dimethyl-N-*p*-toluenesulfonylamidines and N-*p*-toluenesulfonylsulfilimine, respectively.[12] Less reactive, and also less polar, solvents such as chlorobenzene, xylene, and dioxane fail as reaction media probably because they do not dissolve or even swell the sulfonylcarbamate derivative. The most effective solvent for the reaction was found to be pyridine which dissolves the reaction product of *p*-TSI and cellulose as the reaction proceeds. A clear, essentially fiber free, viscous solution of the derivative is formed; this solution can be used in fabrication processes such as film casting or fiber spinning. The effect of the solvent basicity on formation of the derivative was evaluated by running the reaction in triethylamine, a stronger base than pyridine; no reaction was observed. A benzene–pyridine mixture also failed to promote a reaction indicating that not only must pyridine be present for reaction but the solvent mixture must also be able to dissolve the polymer. *p*-Toluenesulfonyl isocyanate was also used neat, *i.e.*, the cotton fibers were completely immersed in *p*-TSI, but no reaction occurred.

The amount of pyridine required for reaction was qualitatively determined. It was learned that as little as 4 ml of pyridine per gram of cellulose is sufficient to promote the reaction. Lower pyridine-to-cellulose ratios will require special techniques for adding the pyridine and the *p*-TSI to the cellulose to obtain a uniform distribution. A clear solution is obtained at concentrations as high as 10 wt % cellulose. Problems were encountered in the purification of the extremely viscous solutions produced by those systems with cellulose concentrations higher than 5–6 wt %. However, it appears from the weight gain of the cellulose that degree of substitution (D.S.) is not effected by the amount of pyridine used as long as the fibers are immersed. This conclusion was confirmed by calculating the degree of substitution on the basis of nitrogen content.

Tertiary amines are normally considered to be catalysts for isocyanate reactions. However, sulfonyl isocyanates form complexes with tertiary amines, which reduce the activity of the isocyanate.[13] The pyridine–*p*-TSI complex exhibits a very low solubility in pyridine and precipitates when *p*-TSI is added to the pyridine–cellulose slurry. Thus the concentration of active species in solution is very low at reaction temperatures below the melting point of the complex. The complex appears to melt around 70° and there is a corresponding increase in the rate of substitution at that temperature. Figure 1 illustrates the degree of substitution attained upon treating cellulose with a 4:1 mole ratio of *p*-TSI–cellulose for 1 hr at various temperatures. The sharp break observed between 70 and 85° demonstrates the rate enhancement produced by dissolution of the molten *p*-TSI–pyridine complex.

The effect of other common isocyanate catalysts was examined but no significant catalytic effects were noted. Dibutyltin dilaurate, reported as the best catalyst for isocyanate reactions, was added in pyridine but no detectable change in reaction rate were observed. Schnell[14] reported that zinc chloride promoted the reaction of aryl isocyanates with cellulose; in our system it was simply a contaminant. The extreme reactivity of sulfonyl isocyanates minimizes the need for a catalyst; a more frequent problem arises in controlling the extremely exothermic addition to any active hydrogen on the substrate.

At 70° the *p*-toluenesulfonyl isocyanate addition proceeded at a rate which could be followed by isolating and analyzing the cellulose derivative. The results (Figure 2) indicate a linear increase in the degree of substitution until a degree of substitution of 2 is reached. At this point the reaction rate becomes considerable slower, probably due to both steric factors and a general decrease in availability of reactive sites. Reproducible initial rates are difficult to obtain due to the heterogeneity of the system so that some scatter in the experimental data is evident. However, there does not appear to be a break in the curve at D.S. 1 which would be expected if primary hydroxyls were reacting more rapidly than secondary hydroxyls as is usually observed in the formation of cellulose derivatives. We plan a more detailed kinetic study of this reaction in a homogeneous system to ascertain the reaction order with respect to *p*-TSI and the activation energy of the process.

Cross-Linking Processes. A cross-linked insoluble resin is preferred for most ion-exchange applications. Treatment of the cellulose derivative with bis(4-iso-

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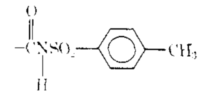
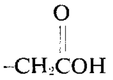
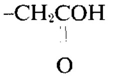
(12) C. King, *J. Org. Chem.*, **25**, 352 (1960).

(13) M. Seefelder, *Chem. Ber.*, **96**, 2343 (1963).

(14) H. Schnell, German Patent 824,039 (1951); *Chem. Abstr.*, **48**, 11058 (1954).

TABLE I

Cellulose derivative	Ionogenic group	Acid properties	Capacity, mequiv/g
Sulfonylcarbamate		Weak acid	2.9
Carboxymethyl	 $-CH_2\overset{\overset{O}{\|}}{C}OH$	Weak acid	0.7[a]
Partial succinate half-ester	 $-CH_2\underset{\underset{O}{\|}}{C}OH$	Weak acid	1.0[a]
Sulfoethylated	$-CH_2CH_2SO_3H$	Strong acid	0.5[a]
Phosphorylated	$-PO_3H_2$	Strong acid	2.6[a]

[a] J. D. Guthrie and A. L. Bullock, *Ind. Eng. Chem.*, **52**, 935 (1960).

cyanatophenyl)methane, *p*-(isocyanatophenyl)sulfonyl isocyanate, chlorosulfonyl isocyanate, dichloroacetic acid, or trichloroacetic acid produces an insoluble cross-linked gel. The cross-linking can be carried out in a concentrated pyridine solution, or the solution can be diluted with DMSO or acetone (solvents) or nonsolvents such as benzene. The porosity of the gel along with the ion-exchange capacity could be regulated by varying in concentration of cross-linking agents as well as the composition of the reaction media. The cross-links produced by dichloro- or trichloroacetic acid were hydrolyzed by 2% NaOH which indicated that ester linkages were produced in addition to the expected acetal information. Cross-links stable to alkaline hydrolysis were produced by the diisocyanates and chlorosulfonyl isocyanate.

p-(Isocyanatophenyl)sulfonyl isocyanate effects gelation within 15 min at 75°. Alkali stable gels are formed at relatively low diisocyanate to cellulose mole ratios which illustrates a high degree of efficiency. The rapid reaction rate, high efficiency, and simultaneous introduction of further acidic sulfonylcarbamate groups combine to make *p*-isocyanatophenylsulfonyl isocyanate an ideal cross-linking agent.

The stability of the cross-links produced by chlorosulfonyl isocyanate was a pleasant surprise. Either esters of urethan-N-sulfonic acids are more stable to alkali than one would anticipate or the cross-linking process proceeds by reaction of the intermediate N-chlorosulfonylurethan with the sulfonylcarbamate moiety to produce stable bonds. Disulfonyl chlorides such as bis(*p*-chlorosulfonylphenyl) ether failed to introduce sufficient cross-links to cause a pyridine solution of the sulfonyl-carbamylated cellulose to gel. Clearly, further research in this area will be required to define precisely the unique properties of chlorosulfonyl isocyanate as a cross-linking agent.

It is also beneficial to control the swelling of the resin used in an ion-exchange system. Since weakly acidic cation exchange resins are generally used at pH's greater than 7, the swelling of the *p*-toluenesulfonyl carbamate derivative in alkali media was minimized by cross-linking. The initial concentration of cross-linking agent per molar equivalent of cellulose was considered to be a measure of the degree of cross-linking introduced into the gel. Degrees of cross-linking effected by 0.05 mol of bis(4-isocyanatophenyl)methane per molar equivalent of cellulose were satisfactory in limiting the swelling of the polymer in neutral to weakly basic systems. However, at pH's above 10 an initial concentration ratio of 0.15 mol/molar equivalent of substrate was necessary to prevent swelling. Cross-link densities of this magnitude did not significantly reduce the ion exchange capacity.

Ion Exchange Characteristics. The ion-exchange properties of the sulfonyl-carbamylated cellulose were investigated to determine the relative acidity as well as the total capacity of a typical resin. The titration curve and the ion-exchange capacity of a typical sulfonylcarbamate derivative with D.S. 2, which had been cross-linked with 0.15 mol of bis(4-isocyanatophenyl)methane per mole of cellulose, were evaluated. The titration curve measured in 0.5 *M* sodium chloride by adding fixed aliquots of 0.1 *N* sodium hydroxide is shown in Figure 3. The shape of the curve illustrates that the sulfonylcarbamate derivatives behave as weak acids.[15]

The total ion-exchange capacity of the resin was determined at pH 10 by the procedure of Guthrie, *et al.*[16] These results are summarized in Table I along with some representative values for other cellulosic cation-exchange resins. The value shown for the sulfonyl-carbamylated cellulose represents an average of several different samples. Capacities higher than those of the

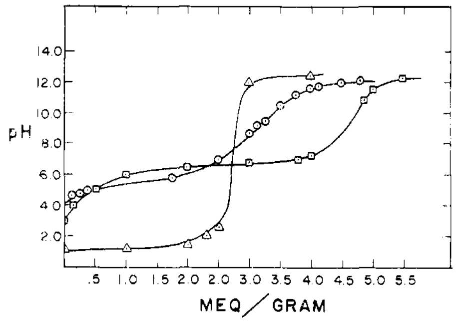


Figure 3. Titration curve of sulfonyl-carbamylated cellulose compared with common acidic ion exchange resins: ○, sulfonyl-carbamylated cellulose; △, polystyrenesulfonic acid; □, cross-linked polymethacrylic acid.

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(15) R. Kunin, "Elements of Ion Exchange," Reinhold Publishing Corp., New York, N. Y., 1960, p 14.

(16) R. B. Benerito, B. B. Woodword, and J. D. Guthrie, *Anal. Chem.*, 37, 1963 (1965).

common cationic cellulose resins were consistently observed.

The superior exchange capacities of the sulfonylcarbamate derivatives can be attributed to several factors. A high degree of substitution can be achieved under relatively mild conditions in contrast to the extreme conditions required to achieve a comparable degree of substitution with the other derivatives. The other derivatives necessarily have a lower degree of substitution to minimize degradation of the cellulose substrate. The uniformity of the substitution also plays an important role. Most of the other derivatives are prepared by a heterogenous process which produces a high concentration of acid sites at the surface but fails to attack the more hindered hydroxide groups within the fiber. Since the reaction of cellulose with *p*-toluenesulfonyl isocyanate becomes homogeneous, an even distribution of the acid sites is achieved and most of the reactive sites have been used efficiently. Finally, the bulky aromatic groups appear to disrupt the crystallinity of the resin; X-ray diffraction indicates a maximum of 10% crystallinity in the noncross-linked resin. Thus the acid sites remain accessible to low molecular weight reagents.

Ion-exchange capacities of cellulose derivatives are limited by the degree of substitution of the ionogenic groups on the substrate. Since the value of the degree of substitution can not exceed 3.0, the theoretical limit on the total capacity is 3.9 mequiv/g. The observed value for the capacity of a resin with D.S. 2 is 2.9 mequiv/g which compares favorably with a calculated capacity of 3.4 mequiv/g. These facts illustrate the relative efficiency of the exchange process as well as the limiting return in the ion-exchange capacity by striving for maximum substitution. In this system an increase in D.S. from 2 to 3 requires a fivefold increase in reaction time, yet this produces a theoretical increase in capacity of only 0.5 mequiv/g.

Ion-exchange capacities are also dependent upon the extent of cross-linking introduced into the resin. The initial mole ratio of cross-linking agent to cellulose was considered to be a measure of the cross-link density and this factor was evaluated. The results obtained on a series of resins with nearly identical degrees of substitution which have been cross-linked with bis(*p*-isocyanatophenyl)methane are [given as moles of diisocyanate per molar equivalent of cellulose, capacity (mequiv/g)]: 0.05, 3.34; 0.10, 3.35; 0.15, 2.90; 0.20, 2.74; 0.30, 2.80.

The maximum capacity observed at low cross-link density is characteristic of cellulosic ion exchange resins; this is apparently due to the initial forced separation of the polymer chains by the cross-linking agent, which makes the ionogenic groups more accessible. Further cross-linking decreases the flexibility of the chains and makes a portion of the acid sites physically inaccessible, thus lowering the observed capacity of the resin. Resins with high cross-link densities are obtained in a granular form suitable for most fixed bed column operations.

Ion exchange resins are of little use if they cannot be regenerated. Regeneration of the sulfonyl-carbamylated cellulose in the acid form can be effected by washing the resin with aqueous hydrochloric acid. When the pH is maintained between 1.0 and 2.0, regeneration is nearly quantitative. The high capacities were retained after several regeneration cycles and no severe degradation of the gel was apparent.

Experimental Section

Reagents. Purified cotton linters were dried over P_2O_5 at 100° *in vacuo* for 24 hr. *p*-Toluenesulfonyl isocyanate was purchased from K and K Laboratories, Inc., and used as received. Chlorosulfonyl isocyanate was obtained from the American Hoechst Corp. and used without further purification. Bis(4-isocyanatophenyl)methane was fractionally distilled *in vacuo;* the major fraction, bp 145–150° (0.2 mm), was recrystallized from hexane. *p*-(Isocyanatophenyl)sulfonyl isocyanate was prepared in 65% yield, bp 120–122° (0.25 mm), by direct phosgenation of sulfanilamide in the presence of butyl isocyanate.[1] The solvents were dried over molecular sieves (4A) or distilled from CaH_2 under nitrogen. All operations involving sulfonyl isocyanates were carried out in a drybox.

Reaction of *p*-Toluenesulfonyl Isocyanate with Cellulose. Ground cotton linters (2.0 g, 0.01235 mol equiv) were charged into a 6-oz beverage bottle and slurried in 150 ml of pyridine. *p*-Toluenesulfonyl isocyanate (6.5 ml, 0.0495 mol) was injected and the bottle sealed under nitrogen with a pressure cap. The mixture was heated in a constant-temperature bath at 80° with intermittent agitation. The cotton linters became highly swollen after 30 min of heating and a viscous solution formed within 2 hr. For applications where D.S. 2 was required the solution was worked up after 3 hr, but the solution can be heated for an additional 18 hr to achieve a maximum degree of substitution. The sulfonylcarbamate derivative was isolated by adding the pyridine solution to 1 l. of ethanol containing 25 ml of concentrated HCl. The supernatant liquid was decanted and the precipitate filtered out as rapidly as possible to minimize alcoholysis of the polymer. The polymer was washed with ethanol in a Waring Blendor to remove the by-products from the excess sulfonyl isocyanate and finally dried at 40° *in vacuo* over P_2O_5. Alternatively, the pyridine solution could be diluted with acetone and the polymer precipitated in benzene or 10% aqueous HCl. Films could be cast directly from the pyridine solution. The degree of substitution was calculated from the weight gain and sulfur content of the polymer. Nitrogen analysis *via* the Kehldahl technique yielded very erratic results, but satisfactory nitrogen assays were obtained by neutron activation analysis. Infrared spectra of films cast from pyridine exhibited the following characteristic absorptions: 3300 cm^{-1} (NH) 1750, 1630 cm^{-1} (carbamate), 1340, 1170 cm^{-1} ($-SO_2-$), 1080 cm^{-1} (–OH). Freshly precipitated polymers with D.S. >1.0 were soluble in 2% sodium hydroxide, dimethyl formamide, dimethyl sulfoxide, tetramethylguanidine, pyridine, tetramethylammonium hydroxide, and ethanolamine. After treatment with dilute acid and careful drying the derivatives could only be dissolved in the strongly basic solvents.

Cross-Linking Procedure. Bis(4-isocyanatophenyl)methane (usually 0.15 mol per mol equiv of cellulose) was added to a 5–6 wt % pyridine solution of the sulfonylcarbamate derivative prepared as described above. The mixture was heated at 75° for 18 hr to form a rigid gel. The gel was purified by grinding in acidic ethanol, washed with ethanol, and finally washed with distilled water until the filtrate was neutral.

Alternatively, the pyridine solution was diluted with benzene and cross-linking was effected in the microgel formed. Samples cross-linked in the presence of a nonsolvent exhibited slightly higher capacities than the samples prepared in the viscous reaction mixture or in dilute solvent mixtures. Attempts to cross-link films immersed in benzene with bis(4-isocyanatophenyl)methane failed.

Evaluation of the alternative cross-linking agents was carried out in pyridine solutions at 75° using 0.15 mol of cross-linking agent per mol equiv of cellulose. The gelation time was considered to be a measure of the reactivity; the following results were obtained [cross-linking agent, time (hr)]: *p*-isocyanatophenylsulfonyl isocyanate, 0.25; chlorosulfonyl isocyanate, 8; dichloroacetic acid, 8; bis(4-chlorosulfonyl phenyl) ether, >48. The cross-links produced by dichloroacetic acid were not stable to alkaline hydrolysis as evidenced by dissolution of 1 g of gel in 2% NaOH after 48 hr at room temperature.

Characterization of the Ion-Exchange Resins. The ion-exchange capacity of these materials was determined by slurrying 1.0 g of the dry polymer in 50 ml of 1.0 *M* NaCl. A known volume of standard NaOH was added. Enough NaOH was added to assure that the pH of the mixture was in the 8–10 range. Finally, the total solution volume was made up to 100 ml with distilled water and the mixture was shaken frequently at room temperature for 48 hr. Aliquots of the supernatant liquid were titrated with standard HCl to the phenolphthalein end point and capacities determined in milliequivalents per gram of dry polymer.

The titration curve was determined by slurrying 1.0 g of dry resin in a mixture of 45 ml of 1 *M* sodium chloride and 45 ml of distilled water and measuring the pH of the mixture until a constant pH value was obtained. Although constant pH values were usually obtained within 0.5 hr, the mixture was stored 4 hr to assure that equilibrium had been established. An aliquot of standard base was then added: the mixture was allowed to equilibrate 1 hr and the new pH recorded. This process was repeated until the addition of base did not change the pH of the mixture. A plot of pH *vs.* milliequivalents of base added per gram of sample was considered the titration curve. The average pK_a, estimated from the pH at half-capacity, was 4.5.

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Multicomponent Polymerization. II. The Effect of Mixing on Copolymerization in Continuous Stirred Tank Reactors[1]

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ABSTRACT: Calculations have been carried out to describe the course of three vinyl copolymerizations which typify free-radical copolymerizations. Conversion of monomer to polymer, and copolymer average composition, as well as copolymer composition distribution (CCD), have been calculated for these three systems in batch reactors (BR) and in continuous stirred tank reactors which have perfect, homogeneous micromixing (HCSTR) or imperfect mixing which leads to segregation on the microscopic scale (SCSTR). The results of the calculations indicate that conversion and *average* composition behavior are not necessarily strongly dependent on mixing in a CSTR, although they are in some systems. However, the CCD is strongly affected by mixing in all systems where the composition drifts with conversion. The magnitude of the effect of mixing on CCD increases with conversion. In the limit a SCSTR gives at high conversion the same CCD as a BR. A HCSTR always gives a monodisperse CCD. Limitations and applications of the calculations are discussed.

1. Polymerization in a CSTR

The use of a continuous stirred tank reactor (CSTR) for linear chain-growth polymerization reactions has much to offer with respect to control of product properties. Denbigh,[2] for example, has shown that in vinyl polymerizations a molecular weight distribution (MWD) can be achieved with a CSTR which is much narrower than that with a comparable batch reactor (BR). In addition it has been shown that molecular weight can be readily modified by appropriate changes in feed rate and composition.

Other advantages are apparent when one considers multicomponent polymerizations. As an example, consider the copolymerization of a mixture of two monomers of unequal reactivity. In a BR the relative supply of the more reactive monomer becomes depleted and the copolymer composition drifts in response to this change. This drift gives rise to a copolymer composition distribution (CCD) ranging from that copolymer composition formed from the initial mixture to those compositions formed in the final stages of reaction. The situation is quite different when the same reaction takes place in an ideal (or homogeneous) CSTR (HCSTR). In this case the depletion of the monomers is compensated for by the feed stream so that a steady-state reaction mixture composition is realized. Aside from statistical variations in copolymer composition, which as shown by Stockmayer[3] become insignificant at high degrees of polymerization, the resulting copolymer is homogeneous in composition.

In many cases this homogeneity or the lack of it can be of great importance. An example is the situation where two pure homopolymers, such as polystyrene and polyacrylonitrile, are incompatible. A physical

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[1] Preceding paper: K. F. O'Driscoll and R. S. Knorr, *Macromolecules*, **1**, 367 (1968).

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