

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Use of Resins Containing Mixed Sulfonic-Acetic Anhydrides as Acylating Agents

Tjoan Liem Ang<sup>a</sup>; H. James Harwood<sup>a</sup>

<sup>a</sup> Institute of Polymer Science The University of Akron, Akron, Ohio

**To cite this Article** Ang, Tjoan Liem and Harwood, H. James(1973) 'Use of Resins Containing Mixed Sulfonic-Acetic Anhydrides as Acylating Agents', *Journal of Macromolecular Science, Part A*, 7: 5, 1079 – 1083

**To link to this Article:** DOI: 10.1080/10601327308060483

**URL:** <http://dx.doi.org/10.1080/10601327308060483>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Use of Resins Containing Mixed Sulfonic-Acetic Anhydrides as Acylating Agents

TJOAN LIEM ANG and H. JAMES HARWOOD

Institute of Polymer Science  
The University of Akron  
Akron, Ohio 44325

### ABSTRACT

Cross-linked polystyrene resins containing acetyl-benzene-sulfonate units were prepared by refluxing acetyl chloride with a commercial sulfonated polystyrene resin. Use of preswelled resin in the acetylation step affords resin in which 50% of the sulfonic acid groups have been acetylated. Although such resins are expected to be powerful acylating agents, they reacted slowly with alcohols larger than ethanol and not at all with aniline. Resins with macroreticular backbones are likely to be more effective as acylating agents than those utilized in the present study.

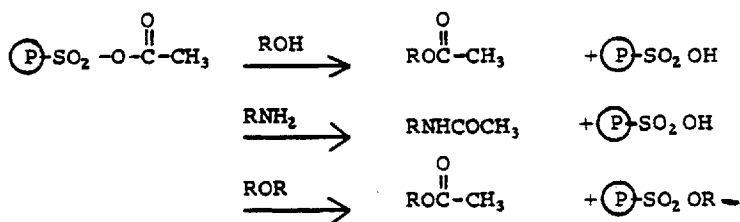
### INTRODUCTION

Resins bonded to acyl derivatives of good leaving groups are useful as mild acylating agents. Columns of such resins can be used very conveniently for conducting acylation reactions, since a solution of substrate need only be passed through the resin to obtain a solution of the pure acyl derivative. The product can then be obtained in pure form and in high yield by simply removing solvent. Cross-linked

resins containing esters of vinylnitrophenol [ 1 ] or N-hydroxymaleimide [ 2 ] units have thus found use in peptide synthesis.

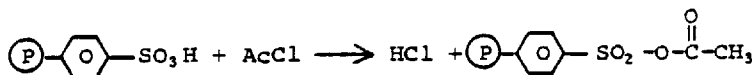
Variations and applications of this approach have only begun to be explored, although valuable synthetic opportunities can be expected to result from studies in this area. In this communication we describe the preparation of cross-linked resins containing mixed sulfonate-acetic anhydride units and their utilization for ester synthesis.

Mixed sulfonic-carboxylic anhydrides, first prepared by Baroni [ 3 ], are reported to acylate phenols, aromatic amines, and alcohols [ 4 ]. The acetyl sulfonates have been used in Friedel-Crafts acylations [ 5 ], and they are such powerful acylating agents that ethers are cleaved by them in high conversion at room temperature [ 6 ]. It thus seemed to us that resins containing acetyl sulfonate linkages could be useful in a number of applications, viz.:



## RESULTS AND DISCUSSION

The procedure of Karger and Mazur [ 6 ] for preparing mixed sulfonate-carboxylate anhydrides was used to prepare a mixed anhydride from a sulfonated polystyrene resin (Amberlite IR-120) and acetyl chloride. The resin was swollen overnight in acetonitrile and was then refluxed with a solution of acetyl chloride in ligroin (bp 60-90°) to obtain a product in which 50% of the sulfonic acid groups were converted to acetyl sulfonate groups.



The relatively low conversion obtained is attributed to difficult accessibility of some of the sulfonic acid groups. It is necessary that the resin be preswollen prior to the acetylation step; only a negligible amount of mixed anhydride was obtained when unswollen resin was

refluxed in acetyl chloride. However, it is desirable that the solvent employed for the acylation step have a limited solubility for HCl, since the acetylation reaction is reversible [4]. Thus the yield of acetyl sulfonate groups was higher when the reaction was conducted in ligroin than when it was conducted in acetonitrile.

Reactions of the acetylated resin with alcohols, phenol, and aniline were then investigated. These studies involved shaking beads of the resin in a substrate-acetonitrile solution. The disappearance of substrate and the appearance of product were monitored by gas phase chromatography. Table 1 lists the approximate times required to obtain complete reactions at room temperature using approximately equimolar amounts of acetylsulfonate units and substrate molecules.

TABLE 1. Reactions of Various Substrates with Acetylated Amberlite IR-120 at Room Temperature Using Acetonitrile as a Solvent for Substrate

Substrate	Product	Time for complete reaction	
		Unswollen resin	Preswollen resin
Methanol	Methyl acetate	0.5 hr	-
Ethanol	Ethyl acetate	0.75 hr	-
1-Propanol	n-Propyl acetate	20 hr	-
2-Propanol	i-Propyl acetate	40 hr	24 hr
1-Butanol	n-Butyl acetate	24 hr	-
2-Butanol	s-Butyl acetate	1 week	48 hr
Isobutanol	i-Butyl acetate	48 hr	-
Cyclohexanol	Cyclohexyl acetate	1 week	-
dl-Menthol	Menthyl acetate	8 days	-
Phenol	Phenyl acetate	a	
Aniline	-	No reaction	
Benzene	-	No reaction	

<sup>a</sup>30% conversion in 1 week.

The reaction rates are very sensitive to substrate size, indicating that steric effects, selective absorption effects, and diffusion rates may influence reactivity significantly. The importance of diffusion effects is

shown by the fact that preswollen resin is more reactive by a factor of 2 or more than is unswollen resin. It seems worth noting that primary alcohols are much more easily acylated than secondary alcohols with these resins. The apparent inactivity of the acetylated resin toward aniline may be due to neutralization of this amine by unacetylated sulfonic acid units present in the resin. Pretreatment of the resins with tertiary amines may be necessary to make them effective for acylation of other amines, but this was not investigated.

In future studies we plan to prepare resins with more accessible sites than are available in those described here. We expect that resins with low degrees of cross-linking [7], macroporous resins [8], or popcorn type resins [9] will be more reactive than those employed in the present study.

## EXPERIMENTAL

Amberlite IR-120 (Rohm and Haas), a sulfonated polystyrene cross-linked with 8% divinylbenzene, 20-50 mesh, in the  $H^+$  form, was dried in a vacuum oven at  $110^\circ$  for 20 hr. The capacity of the dried resin was 5.28 meq/g as determined by reacting the resin with excess alkali and backtitrating the excess alkali with acid.

### Acetylation of the Sulfonic Acid Resin

(a) A small portion of the dry resin (2 g,  $\sim 10$  meq) was weighed to the nearest 0.1 mg and stirred in a refluxing mixture of acetyl chloride (8 g, 0.1 mole) and ligroin (15 ml, bp  $60-90^\circ$ ) for 6 hr. The resin was washed three times with 10 ml portions of ligroin, then two times with a 50:50 ligroin-chloroform mixture. It was then dried by gentle heating on a hot plate. The resin was stirred with standard 0.2 N KOH solution (100 ml) for 2 hr at room temperature. Titration of unconsumed KOH with standard  $H_2SO_4$  indicated the capacity of the resin to be 5.29 meq/g. From this result it was concluded that the extent of acetylation obtained was 0.2%.

(b) Procedure (a) was repeated using dry resin that had been allowed to swell in acetonitrile for 12 hr. The extent of acetylation obtained, as determined by reaction with KOH, was 50.2% (apparent capacity = 7.93 meq/g). About 100 g of the mixed anhydride resin was prepared by this method. The anhydride resin was dried in a vacuum oven for 1 hr at  $90^\circ$  and at  $70^\circ$  overnight. The resin swelled [10] only 17% in acetonitrile as contrasted to the original resin which swelled 49% in this solvent.

(c) Procedure (b) was repeated using preswollen resin and using acetonitrile as the solvent instead of ligroin. The extent of acetylation was 39.2% (apparent capacity toward KOH = 7.35 meq/g).

Acetylation Experiments

Resin samples (2.5 g, containing ~6 meq of acetylsulfonate) and 0.2 M solutions of substrate in acetonitrile (2.5 ml, 5 meq of substrate) were introduced into 4 ml vials and the mixtures were shaken at room temperature. The reaction mixtures were sampled periodically and were analyzed by gas phase chromatography for the presence of starting and final products. In all cases the identity of the final product was established by comparing its retention time with that of authentic material. The reaction was considered complete when no substrate was detected. Reactions involving methanol and ethanol were sampled every 15 min. Other reactions were sampled every 1-6 hr, except for extremely slow reactions which were sampled every 12 hr. These sampling rates should be kept in mind when considering the significance of the times required for complete reaction that are listed in Table 1.

## REFERENCES

- [ 1 ] M. Fridkin, A. Patchornik, and E. Katchalski, J. Amer. Chem. Soc., **88**, 3164 (1966).
- [ 2 ] D. A. Laufer, T. M. Chapman, D. I. Marlborough, V. M. Vaidya, and E. R. Blout, Ibid., **90**, 2696 (1968).
- [ 3 ] A. Baroni, Atti Accad. Naz. Lincei, Rend., Cl. Sci. Fis. Mat. Nat., **17**, 1081 (1933); Chem. Abstr., **28**, 1661 (1934).
- [ 4 ] C. G. Overberger and E. Sarlo, J. Amer. Chem. Soc., **85**, 2446 (1963).
- [ 5 ] G. A. Olah and S. J. Kuhn, J. Org. Chem., **27**, 2667 (1962).
- [ 6 ] M. H. Karger and Y. Mazur, J. Amer. Chem. Soc., **90**, 3878 (1968).
- [ 7 ] R. B. Merrifield, Ibid., **85**, 2149 (1963).
- [ 8 ] J. Seidle, J. Malinsky, K. Dusek, and W. Heitz, Fortschr. Hochpolymer. Forsch., **5**, 113 (1967).
- [ 9 ] R. L. Letsinger, M. J. Kornet, V. Mahadevan, and D. M. Jerina, J. Amer. Chem. Soc., **86**, 5163 (1964).
- [ 10 ] G. W. Bodamer and R. Kunin, Ind. Eng. Chem., **45**, 2577 (1963).

Received for publication January 29, 1973