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## **Polymers and Copolymers of Unsaturated Tetrahydropyranyl Esters**

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### **ABSTRACT**

The preparation and deesterification of a number of polymers and copolymers of unsaturated tetrahydropyranyl esters has been studied. The conditions required to remove the tetrahydropyranyl group from these esters are extremely mild. Hence it is possible to use dihydropyran as a protecting group in the preparation of polymers containing other groups susceptible to normal hydrolysis conditions. The reactivity ratios for the tetrahydropyranyl methacrylate/styrene and tetrahydropyranyl acrylate/styrene copolymerization systems have also been determined.

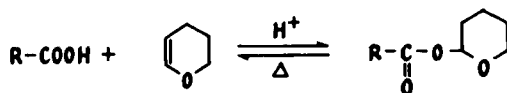
### **INTRODUCTION**

There are situations in which it is neither possible nor desirable to prepare polymers or copolymers of unsaturated acids by polymerization of the acid monomers. For example, in a monomer mixture where acid catalyzed interaction occurs between the monomers, it is necessary to mask the carboxyl group and to liberate the free acid

at some later stage. Similarly some acid monomers or the polymers and copolymers derived from them have undesirable solubility characteristics and the use of a derivative of the acid can overcome this problem.

Previous attempts to mask acid groups have been mainly directed toward converting the acid monomers to esters or amides. However, while these derivatives of some polyacids are relatively easy to hydrolyze [1], the polymethacrylic esters and amide are often stable [1-4]. Severe conditions are required to achieve even appreciable hydrolysis of these polymers and rarely is it possible to achieve complete conversion to the free acid. Even in cases where the ester or amide group can be removed, the conditions required are such that other labile groups present in the polymer may also be cleaved.

Some time ago, dihydropyran was used as a protecting group for various carboxylic acids used in the preparation of a number of ketones [5, 6]. This particular protecting group was chosen because it was found that the esters were thermally unstable, being converted to the required acid and dihydropyran at elevated temperatures:



The use of dihydropyran as a masking group for unsaturated acids has been studied [7] only briefly. Tetrahydropyranyl (THP) methacrylate and acrylate were prepared, copolymerized with various acrylic and methacrylic monomers, and the masking group removed during drying of films of these polymers at 150°C.

Because of their thermal instability these esters have a number of attractive possibilities for their further use as protecting groups, especially where other groups susceptible to normal hydrolysis conditions are present in the polymer.

This paper presents a study of the preparation and deesterification of THP acrylate, methacrylate, maleate, and itaconate polymers and copolymers. The measurement of the reactivity ratios for the THP acrylate/styrene and THP methacrylate/styrene systems is also described.

## RESULTS AND DISCUSSION

### Preparation and Deesterification of Poly-THP Esters

THP acrylate and methacrylate were prepared, in high yields, by the addition of the appropriate acid to an excess of dihydropyran in the

presence of a trace of p-toluene sulfonic acid. Heating the esters in the absence of solvent resulted in deesterification taking place at 121°C for THP acrylate and 145°C for THP methacrylate, the products being the parent acid and dihydropyran.

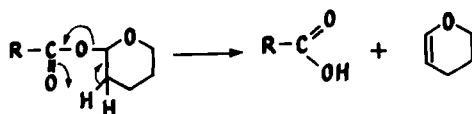
The diesters of maleic and itaconic acid were formed in a similar manner to the above esters but the preparations proved more difficult, reaction times being longer and yields lower.

The polyacrylate and polymethacrylate were readily prepared by heating the monomer in benzene with azodiisobutyronitrile. Thermogravimetric analysis established that the dry polymers deesterified at 120 and 145°C for poly-THP acrylate and for poly-THP methacrylate, respectively.

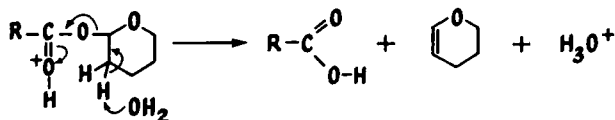
THP maleate and THP itaconate were copolymerized with styrene using the same conditions as for polymerization of the acrylates, deesterification taking place at 125 and 120°C for the maleate and itaconate, respectively.

In each case, deesterification takes place under much milder conditions if water is present, typical reaction conditions using water as a solvent being 70°C for 24 hr. These conditions are much less severe than those used to cleave most other protecting groups. Titration of the resulting polymers showed that all the protecting groups had been removed, even from the hindered methacrylate polymer. The deesterification reaction is enhanced by the presence of a small amount of strong mineral acid, reducing reaction times to 2 hr.

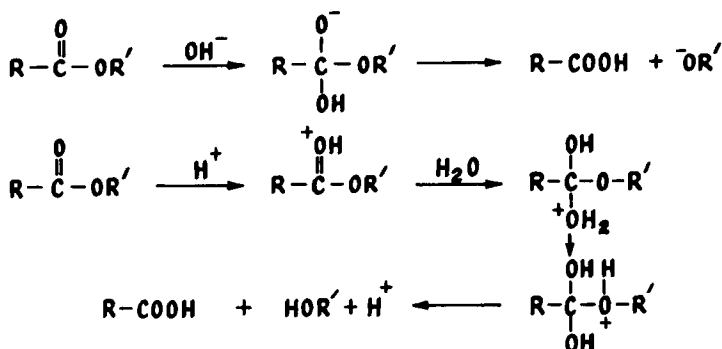
The ease with which all the ester groups are removed reflects the nature of the reaction mechanism, which probably involves a cyclic intramolecular rearrangement:



Acidic conditions would lead to protonation of the carbonyl oxygen, thereby assisting the cleavage of the oxygen-carbon bond:



These mechanisms require no approach of any species to the crowded carbonyl carbon atom, as is necessary in the acid or base hydrolysis of esters:

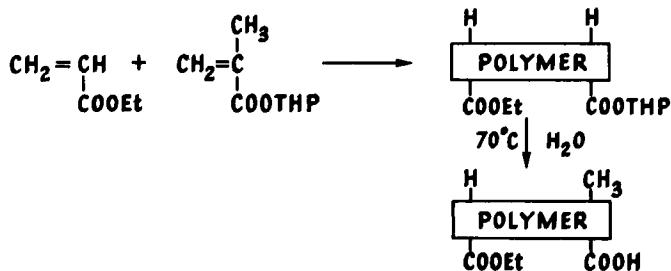


### Copolymers of THP Methacrylate

The mild conditions used for removing THP ester groups are unlikely to affect most other groups which are susceptible to normal hydrolysis conditions. Hence these protecting groups have potential use in the preparation of a number of copolymers. To illustrate its use, copolymers of THP methacrylate/methyl methacrylate and THP methacrylate/ethyl acrylate were prepared using azodiisobutyronitrile as the initiator. NMR spectroscopy showed that each copolymer contained the same relative amount of each ester as was present in the monomer mixtures.

Heating the copolymers in aqueous ethanol at 70°C for 24 hr produced polymers which, in each case, had acidic groups equal to the number of THP methacrylate residues in the original polymers. NMR spectroscopy showed the absence of THP ester groups in both cases.

The ethylacrylate/THP methacrylate copolymer shown below demonstrates the unique feature of this particular protecting group. Most other protecting groups would necessitate the use of acidic or basic conditions to liberate the carboxylic acid and this would also bring about hydrolysis of the ethyl acrylate residues.



It can be concluded that it is possible to remove THP protecting groups from a copolymer without affecting other labile groups which are present.

### Cross-Linked Polymers

Cross-linked polyacrylic acids are often used in ion-exchange applications. To test the effectiveness of dihydropyran as a masking group in such systems, poly-THP methacrylate cross-linked with 3% ethylene glycol dimethacrylate was prepared. Heating the polymer in water at 80°C for 24 hr resulted in the quantitative release of acid groups as determined by electrometric titration. Further study on the use of masked acid monomers in the preparation of ion-exchange resins is in progress.

### Reactivity Ratios

If THP groups are to be used as protecting groups, it is desirable to determine the reactivity ratios for the protected acid monomers in order to be able to calculate monomer distributions in copolymers. The THP methacrylate/styrene and THP acrylate/styrene copolymer systems were chosen for reactivity ratio measurements. Approximate ratios for THP methacrylate and styrene were found by the Fineman and Ross [8] technique. More accurate determinations for both copolymer systems were made using the method from a recent publication by Francis, Solomon, and Spurling [9].

### Fineman and Ross Determination

A number of monomer mixtures of various compositions were polymerized to low conversions. The compositions of the resulting polymers were determined by microanalysis.

Using the approximate relationship

$$\frac{f-1}{F} = -r_2 \left( \frac{f}{F^2} \right) + r_1$$

where  $F = (M_1/M_2)$  and  $f = (m_1/m_2)$  [ $M_1, M_2$  refer to the monomer composition and  $m_1, m_2$  refer to the polymer composition], the values for the reactivity ratios  $r_1$  and  $r_2$  were found to be 0.50 and 0.47, respectively, where THP methacrylate is monomer 1 and styrene is monomer 2 (Fig. 1).

### Francis, Solomon, and Spurling Method

The derivation of the Fineman and Ross equation uses approximations that may introduce relatively large errors into the reactivity ratios calculated by this method. Recent work by Francis, Solomon, and Spurling uses a more accurate method for reactivity ratio determination.

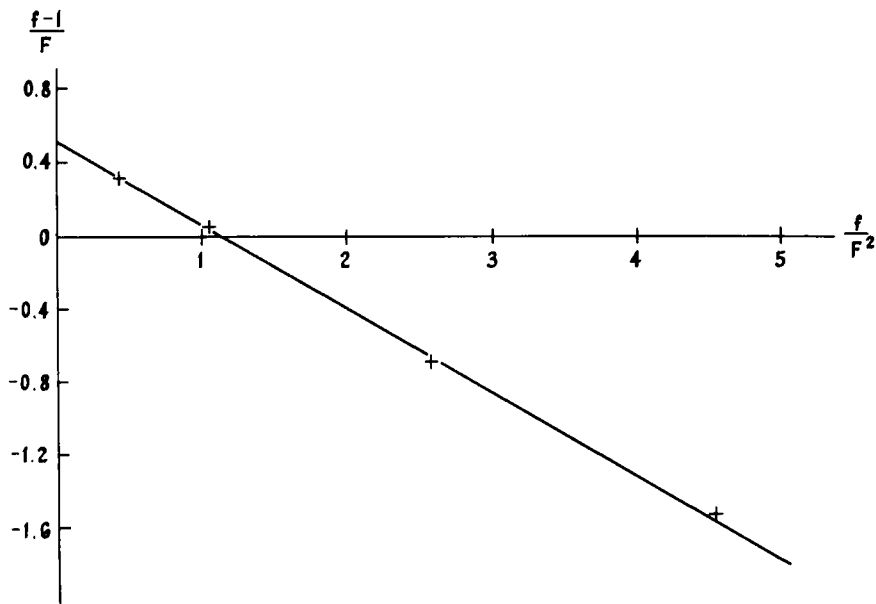


FIG. 1. Fineman and Ross plot for THP methacrylate/styrene copolymerization.

This method requires the polymerization of different monomer mixtures and the determination of the polymer composition for each at a number of different conversions. The conversions and polymer compositions were determined by GLC analysis of the monomers in the reaction mixture and by gravimetric and microanalysis techniques, good agreement being obtained between the two methods.

The results were analyzed using a completely numerical procedure based on the equation of Skiest [10]. The degree of conversion is given by

$$D = 1 - \exp\left(\int_{(f_1)_0}^{f_1} \frac{df_1}{F_1 - f_1}\right)$$

where  $F_1$  is the mole fraction of monomer 1 in the increment of copolymer formed at a given stage in the polymerization and  $f_1$  is the mole fraction of that component in the feed. The experimental procedure measures values of  $(f_1)_0$ ,  $f_1$ , and  $D$ . The value of  $D$  is calculated from the above equation for various values of  $r_1$  and  $r_2$ , thus enabling

the best values for the reactivity ratios to be found. This method is valid for all degrees of conversion.

Using the above procedure, the reactivity ratios of Table 1 were determined.

TABLE 1. Reactivity Ratios

Monomer 1	Monomer 2	$r_1$	$r_2$
THP methacrylate	Styrene	0.59	0.42
THP acrylate	Styrene	0.13	0.53

The Price-Alfrey [11] Q-e values were calculated from the reactivity ratios assuming the values of  $Q_2 = 1.0$  and  $e_2 = -0.8$  for styrene (Table 2).

TABLE 2. Q-e Values

Monomer	Q	e
THP methacrylate	0.923	0.381
THP acrylate	0.510	0.835

## EXPERIMENTAL

### Preparation of THP Acrylate and Methacrylate

Tetrahydropyranyl acrylate and methacrylate were prepared by the published methods [7] and distilled under reduced pressure to give analytically pure compounds.

### Preparation of THP Maleate

A solution of maleic acid (10 g,  $8.6 \times 10^{-2}$  moles), dihydropyran (21.7 g,  $2.58 \times 10^{-1}$  moles), and p-toluene sulfonic acid (10 mg) in dimethoxyethane (20 ml) was stirred at room temperature for 16 hr. The solution was shaken with solid sodium bicarbonate, filtered, and



the solvent and excess dihydropyran removed under reduced pressure.

Attempts to distill the ester under reduced pressure resulted in decomposition.

The structure of the undistilled product was confirmed by NMR and IR spectroscopy.

NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  = 6.25 singlet (2H), 6.10 multiplet (2H), 3.80 multiplet (4H), and 1.70 multiplet (12H). The NMR spectrum also showed the presence of some fumarate ester.

The IR spectrum contained a carbonyl band at  $1725\text{ cm}^{-1}$  but no carboxylic acid bands.

### Preparation of THP Itaconate

THP itaconate was prepared in 55% yield by the above procedure except that benzene was used as the solvent.

The ester readily decomposed and distillation was not possible. The structure of the undistilled ester was confirmed by NMR and IR spectroscopy.

NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  = 6.39 singlet (1H), 6.02 multiplet (2H), 5.76 singlet (1H), 3.75 multiplet (4H), 3.40 singlet (2H), and 1.66 multiplet (12H).

The IR spectrum contained a carboxyl band at  $1725\text{ cm}^{-1}$  but no carboxylic acid bands.

### Polymerization of THP Acrylate and Methacrylate

The monomers, as 10% solutions in benzene, were polymerized at  $70^\circ\text{C}$  for 16 hr using azodiisobutyronitrile (1%) as the initiator. The polymers were precipitated in petroleum spirit, at low temperatures in the case of the polyacrylate.

Yields in each case were greater than 90%.

### Copolymerization of THP Maleate and Itaconate with Styrene

Copolymers of THP maleate/styrene 1:2 (by weight) and THP itaconate/styrene 1:2 (by weight) were prepared and isolated by the same procedure used to obtain the THP acrylate homopolymers.

### Preparation of Copolymers of THP Methacrylate

Copolymers of THP methacrylate/methyl methacrylate 1:4 (by weight) and THP methacrylate/ethyl acrylate 1:4 (by weight) were

prepared by the method used to obtain the homopolymers of THP methacrylate.

### Preparation of Cross-Linked Poly-THP Methacrylate

A solution of THP methacrylate (10 g,  $5.9 \times 10^{-2}$  moles), ethylene glycol dimethacrylate (0.35 g,  $1.77 \times 10^{-3}$  moles), and azodiisobutyronitrile (0.1 g) in benzene (25 ml) was degassed and heated at  $70^{\circ}\text{C}$  for 16 hr under nitrogen. The product was washed with acetone, filtered, and dried under reduced pressure to give the required insoluble polymer in 60% yield.

### Deesterification of Poly-THP Esters

#### Homopolymers

A weighed amount of the homopolymer was dispersed in distilled water and heated at  $70^{\circ}\text{C}$  for 24 hr, during which time the polymer slowly dissolved to form a clear solution. The acid content of the polymer was determined by titration with 0.1 M NaOH solution.

#### Copolymers

A weighed amount of the copolymer was dissolved in aqueous ethanol (90%) and heated at  $70^{\circ}\text{C}$  for 24 hr. The polymer solution was titrated with 0.1 M alcoholic KOH solution.

### Cross-Linked Poly-THP Methacrylate

A number of samples of polymer were accurately weighed into small screw-top containers, an equal volume of distilled water was added to each, and the closed containers were heated at  $80^{\circ}\text{C}$  for 24 hr. Various aliquots of 0.1 M NaOH solution were added to the containers which were then shaken overnight at room temperature. After standing for 30 min, the pH of each solution was measured. The resulting titration curve indicated that the deesterification was quantitative.

### Reactivity Ratios

#### Fineman and Ross Technique for THP Methacrylate/Styrene Copolymerization

Reagents. Styrene was washed free of inhibitor with 1 M sodium hydroxide, dried over sodium sulfate, and distilled under reduced pressure in an atmosphere of nitrogen.

THP methacrylate was freshly prepared and distilled under reduced pressure prior to use.

Benzene was dried over molecular sieves and distilled at atmospheric pressure.

Azodiisobutyronitrile was obtained from Fluck and used without further purification.

**Copolymerization Procedure.** A solution of THP methacrylate and styrene in benzene in the appropriate proportions, depending on the initial monomer concentration required (e.g. 3.28 g THP methacrylate and 2.00 g styrene in 10.56 g of benzene), was added to a flask containing azodiisobutyronitrile (1%). The vessel was purged with nitrogen, sealed, and heated at 70°C for the appropriate time. The polymer solutions were immediately poured into a vigorously stirred quantity of petroleum spirit and the polymer was collected by filtration.

The composition of the polymer was determined from the micro-analysis figures.

This procedure was repeated for other solutions of different monomer compositions (see Table 3).

TABLE 3. Polymer Composition vs Feed Composition for Fineman and Ross Determination

Mole fraction of THP methacrylate in monomer mixture	Conversion	Micro-analysis		Mole fraction of THP methacrylate in polymer	
		Av C	Av O	Based on C	Based on O
0.250	9.0	79.4	12.9	0.324	0.340
0.333	7.1	77.4	14.6	0.390	0.392
0.500	2.5	74.1	17.9	0.509	0.574
0.667	4.0	71.1	20.1	0.635	0.620

Francis, Solomon, and Spurling Technique for THP Methacrylate/Styrene and THP Acrylate/Styrene Copolymerizations

**Copolymerization Procedure.** A 100-cc flask was fitted with a stirrer, suba seal, and nitrogen inlet and outlet tubes. The flask was charged with the appropriate monomer mixture (e.g., 8.45 g THP methacrylate, 1.55 g styrene) and benzene (15.0 g). Azodiisobutyronitrile (0.10 g) was added and the solution was heated at 70°C with stirring in an oil bath, while maintaining a nitrogen atmosphere above the solution.

Samples were withdrawn at regular intervals and immediately cooled in ice.

Analysis of samples. Gas-liquid chromatography. A gas chromatograph model Pye Series 104 equipped with a flame ionization detector was used. The  $\frac{1}{4}$  in.  $\times$  5 ft column was packed with 10% SE 30 on Gaschrome Z.

In order to separate the polymer present in samples, a 6-cm glass precolumn packed with 10% SE 30 on Gaschrome Z was used. A freshly packed precolumn was used for every run.

Sample size was 0.5  $\mu$ liter.

Because of the thermal instability of the esters, the use of high temperatures had to be avoided, column and inlet port temperatures of 115 and 110°C being used for the methacrylate and acrylate, respectively.

It was shown that a straight line relationship existed between monomer concentration and peak height for the three monomers used, except at high concentrations where there was a departure from linearity, especially in the case of styrene. All the experimental samples were diluted with benzene to bring the residual monomer concentrations into the linear range.

The GLC results are shown in Tables 4 and 5.

Gravimetric and elemental analysis. The samples from the THP methacrylate/styrene copolymerization were poured into a large volume of petroleum spirit and the precipitated polymer collected

TABLE 4. Conversion/Composition Correlation for THP Methacrylate/Styrene Copolymerization

Mole fraction of THP methacrylate in feed	Conversion (%)	Mole fraction of THP methacrylate in polymer
0.770	0	-
0.784	20.9	0.642
0.808	30.75	0.608
0.811	59.60	0.669
0.815	80.10	0.686
0.829	85.60	0.689
0.250	0	-
0.248	10.1	0.250
0.230	22.0	0.323
0.207	30.2	0.350
0.184	41.2	0.329
0.183	46.5	0.328
0.177	53.9	0.318
0.152	62.5	0.308

TABLE 5. Conversion/Composition Correlation for THP Acrylate/Styrene Copolymerization

Mole fraction of THP acrylate in feed	Conversion (%)	Mole fraction of THP acrylate in polymer
0.500	0	-
0.522	14.9	0.373
0.524	29.9	0.443
0.557	35.5	0.397
0.561	49.7	0.439
0.576	53.5	0.439
0.591	62.0	0.445
0.592	64.6	0.451
0.1000	0	-
0.0905	12.6	0.165
0.0854	20.3	0.157
0.0830	31.3	0.137
0.0757	37.6	0.133
0.0732	46.6	0.130
0.0685	55.0	0.126
0.0606	59.8	0.126
0.0551	63.1	0.126

and weighed. Elemental analysis was carried out by the Microanalytical Laboratory of the Division of Applied Chemistry.

Conversions and polymer compositions determined by this method were not significantly different from those obtained by the GLC method.

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