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Stereoregular Copolymers of Methacrylic Acid and of Methyl Methacrylate

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SUMMARY

Different techniques and mechanisms of hydrolysis of isotactic, syndiotactic, and atactic PMMA are compared for over-all rates and reaction yields. A combined hydrolysis using a mixture of hydriodic and acetic acid gave the best results, and included the conservation of tacticity and size of the acid-ester copolymers obtained. These conclusions have been confirmed recently by several operators.

INTRODUCTION

Stereochemical studies of polymethacrylic acids have been developed during the past decade due to the direct polymerizations accomplished by Bovey [1] and by Loebel and O'Neill [2], to the studies of Loebel and O'Neill [3], and to the more recent research of Nagasawa [5], Matzusaki [6], and Tsuruta [7] and their colleagues. The creation of a polymer of methacrylic acid (PMA) whose isotacticity approaches 100% has had to proceed through the synthesis of a corresponding ester and its subsequent hydrolysis.

Our main objective was to evolve a method which, on the one hand made use of a gradual hydrolysis and, on the other, did not degrade the polymer nor alter its tacticity. Our interest in the polyelectrolyte copolymers resulting from these preparations has been described briefly [8]. It seems

justifiable to us to communicate the results we obtained by different methods of hydrolyzing stereoregular poly(methyl methacrylates) (PMMA).

The different techniques of hydrolysis we used can be classified in the four following groups: 1) alkaline hydrolysis; 2) hydrolysis by strong acids; 3) transesterification; and 4) combined hydrolyses through a) organic acid followed by weak base attack, and b) simultaneous strong acid hydrolysis and transesterification.

EXPERIMENTAL

Alkaline Hydrolysis

This is an industrial method [10] which has been studied in detail both in heterogeneous phase by Glavis [11], and in homogeneous phase by Smets [12].

The generally accepted mechanism includes the following two steps: an internal rearrangement giving a 6-member ring by interaction of an ester group with an undissociated acid group or a carboxylic group; this is followed by an external attack of a hydroxide ion.

The importance and relative speed of these two steps is dependent on the pH and on the degree of hydrolysis [13, 14].

a) In a heterogeneous phase (KOH-isopropyl alcohol). We have confirmation of the greater speed of the hydrolysis of the isotactic polymer than of the other two.

In 48 hr, the limit of hydrolysis is attained with a yield of 78-80%, in agreement with Glavis. We found no progress of the hydrolysis for any of the three structures even after 340 hr.

b) In a homogeneous phase (reflux heating of solutions of polymers already 75-80% hydrolyzed). The new limit of hydrolysis becomes 85% for each structure; it is attained quite rapidly and does not increase even after 250 hr of reflux heating.

It seems that the upper limit of the yield of the reaction with OH^- attack, due to a kinetic or a steric hinderance, if not to mechanism, is 85%. It is to be observed that this limit is very close to the well-known theoretical one calculated by Flory for topochemical reactions acting spontaneously on two nearby functions.

Hydrolysis by Strong Acids

This technique has been described by Smets and De Loecker [4] as well as by Loebel [2], and Miller [15] has also proposed some variations.

The accepted mechanism is similar to that of the alkaline hydrolysis.

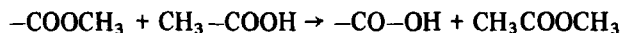
The method of Miller [15], which uses hydrochloric acid with the tert-butyl ester of PMA, is inefficient with PMMA in dioxane-water solution.

The method of Smets [4], in which the polymer is dissolved in concentrated sulfuric acid, gave us stereoregular polyacids with a maximum yield of 85% at 60°C, as at 20°C. On the basis of our final titration, 100% hydrolysis was never obtained with PMMA without degradation. In our experiments, in air or under nitrogen, the more hydrolyzed products were dark brown or black even after several purifications; the syndiotactic ones were green. Tsuruta [7] has made similar observations.

The order of reactivity remains the same as in the alkaline hydrolysis: the rate of hydrolysis decreases in the order isotactic > atactic > syndiotactic.

Transesterification

As described by Katchalsky [16], the equation for transesterification with acetic acid is:



p-Toluene sulfonic acid is used as catalyst.

The transfer of the alcohol residue from the polyester to the monomeric acid can be an advantage in limiting the reesterification of the polyacid. The original paper indicated an 85% yield in 18 hr; we obtained an 88% yield in 60 hr.

There is a principle according to which a transesterification is easier when the number of carbons of the originally free acid is smaller than in the alcohol residue to be transferred [16]; so we tried using formic acid instead of acetic. There was no change in the yield, but its upper limit was attained after only 24 hr.

Combined Hydrolyses

We envisaged two techniques of combined hydrolysis:

a) Successive hydrolyses with change of the attacking group. As mentioned

Table 1. Results of Hydrolysis of Poly(methyl

Polymers	Tacticity coefficient J of Goode (from IR)	Molecular weight (\bar{M}_p)	Alkaline hydrolysis			
			Heterogeneous		Homogeneous	
			Time (hr)	p (% yield)	Time (hr)	p (% yield)
A ₁	98.4					
A ₂	97.2		2	18		
A ₃	98.1					
A ₄	99.5	280,000	24	58	250	85.1
S ₄	112		2	20.2		
S ₅	113		24 48	56.2 79.6	250	84.8
S ₆	108	960,000				
I ₁	35.1					
I ₂	34.3					
I ₃	30.1		15	48		
I ₄	29	500,000	24	68		
I ₅	29.2		2 48	32 78.2	250	85.4

methacrylates) by Use of Various Techniques

Acid, H ₂ SO ₄		Transesterification				Mixed IH/CH ₃ COOH (48 hr)
Time (hr)	p (%) yield)	CH ₃ COOH		HCOOH		
		Time (hr)	p (%) yield)	Time (hr)	p (%) yield)	
24 (20°C)	83.4	24	32	18	28	
1 (60°C)	82.7	62	87.6	24	87.8	
1 (60°C)	87.5					89.2
64 (20°C)	88.4					89.8
24 (20°C)	79.8	24	38.4			
1 (60°C)	77.3			18	33	88.1
60 (20°C)	74.7	58	86.2	24	86.4	89.6
						90.2
14 (60°C)	56.8			18	66	
		24	46.3			
24 (20°C)	73.4			24	88.6	89.7
24 (20°C)	66.5					
62 (20°C)	87.2	60	88.2	24	87.9	

before, hydrolysis by formic acid of PMMA gives an 87-88% yield in 24 hr. These polyacid-polyester copolymers were submitted to an alkaline attack of 230 hr duration in normal KOH under reflux. After purification, the product obtained contained 93% acid groups.

It can be proposed that this progress is due to a change in the mechanism. First, in acid medium protons attack the oxygen of the alcohol, and then the hydroxide ions in basic medium attack the carbon from the other side of the ester group. It can be noted that we have already obtained a marked progress in the yield of otherwise incomplete reductions of polyketones by using different metal hydrides in opposition to the repetitive use of the same hydride [18]. Both of these cases show the possibility of a change in the mechanism of attack. However, in the present hydrolysis, the gain in acid groups was accompanied by an alteration of molecular weights and structures.

b) Simultaneous combination of strong-acid hydrolysis and transesterification. Heated to 80°C for 48 hr in sealed tubes with a mixture of hydriodic and acetic acids, PMMA is hydrolyzed with a yield of 90%. This is somewhat higher than when either of the two acids are used alone.

The great interest of this last technique is that it causes no detected alteration of mass or tacticity. This has been confirmed by several operators in both our own or other laboratories.

Determinations of the degree of hydrolysis were made by potentiometry and tacticities were controlled by IR spectra of the esters obtained by re-methylation according to the procedure of Katchalsky [16].

CONCLUSION

The limits found for the hydrolyzed ester groups of PMMA of all tacticities are 78% in heterogeneous alkaline medium, 85% in homogeneous alkaline phase, 80-85% in concentrated H₂SO₄ (where a degradation of mass and structure was observed), 0% with HCl in water-dioxane, 80% with HI, 87% by transesterification with CH₃COOH or more quickly with HCOOH, 93% with acid followed by alkaline attack (but also with alteration of structure and mass), and 90±1% with mixed HI and CH₃COOH without degradation.

Techniques and results are summarized in Table 1.

On the basis of these experiments, nondestructive hydrolysis has an upper limit of 90% for all stereoregular or atactic PMMA. This limit could well be due to the necessity of forming 6-membered anhydride cycles which are generally accepted in the hydrolysis mechanism.

We have already published some results on the polyelectrolytic properties of acid-ester copolymers obtained by mixed acidolysis [8]. Kinetic data of hydrolysis together with other results on the properties in solution will be communicated in the next paper [19].

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