The Acid Hydrolysis of Isotactic and Syndiotactic Poly(methyl methacrylate)[1a]

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ABSTRACT: Isotactic and syndiotactic poly(methyl methacrylate) (PMMA) were partially hydrolyzed in concentrated sulfuric acid. The distribution of the carboxylic acid residues in the isotactic copolymers was determined by thermally dehydrating the acid to cyclic anhydride groups and comparing the yield of anhydride with the conversion calculated for random, block, and random pair distribution models; a strong tendency toward blocking was found. The proton resonance spectra of similar samples of the syndiotactic copolymers, reported previously by Klesper, indicated a random sequence distribution. The difference in the distribution of the carboxylic acid units in materials derived from the polymers suggested a mechanistic explanation for the differences in the maximum degree of hydrolysis and the relative rates of the hydrolysis reactions. The failure of syndiotactic PMMA to hydrolyze beyond about 85% could be explained by the deactivation in otherwise random hydrolysis of ester units flanked on both sides by pairs of methacrylic acid residues (or anhydride rings). The autocatalytic effect demonstrated by the formation of blocks of acid residues during the hydrolysis of ester groups in the isotactic polymer is shown to account for both the faster rate and the completion of hydrolysis.

Previous investigators[2] have reported that isotactic and syndiotactic poly(methyl methacrylate) (PMMA) differ in their ease of hydrolysis in sulfuric acid. In concentrated sulfuric acid, the isotactic polymer is hydrolyzed completely in about 1 hr at 55° to poly(methacrylic acid) (PMAA) while highly syndiotactic polymer is hydrolyzed at a much slower rate to a limiting conversion of 85 mol % in 24 hr or longer. The purpose of this paper is to present a physical explanation for this difference in the maximum extents of hydrolysis for the two stereoregular forms of PMMA.

It is well known that acid-catalyzed hydrolysis of low molecular weight esters is an equilibrium reaction. If the concentration of water is relatively small and the alcohol by-product is not removed from solution, the equilibrium constant might not be large enough to permit virtually complete hydrolysis of the ester. The failure of highly syndiotactic PMMA to hydrolyze beyond 85% cannot be explained by such an equilibrium process, since no additional hydrolysis occurs when the copolymer is redissolved in fresh, methanol-free sulfuric acid.

When both isotactic and syndiotactic PMMA are hydrolyzed in hydroiodic acid at 140°, the resulting polymers contain acid anhydride rings.[3] Although no attempt was made to obtain complete or limiting degrees of hydrolysis (the rate is extremely slow[3]), the presence of anhydride is of interest. If the hydrolysis reaction proceeds randomly and exclusively in pairs (directly through the cyclic anhydride), then the maximum conversion expected is about 86 mol %[4] which is very nearly the extent of hydrolysis observed for syndiotactic PMMA hydrolyzed in sulfuric acid. We have examined the distribution of methacrylic acid residues in partially hydrolyzed PMMA to determine if the mechanism of the reaction in concentrated sulfuric acid differs for the two stereoregular forms.

Our mode of analysis is as follows. If the partially hydrolyzed copolymer is heated, adjacent acid groups eliminate water to form intramolecular anhydride rings. Since the fraction of acid groups dehydrated depends upon the distribution of the methacrylic acid residues in the polymer, the type of sequencing of the residues in the partially hydrolyzed PMMA is determined by comparing the experimental anhydride content of the heated polymers with that calculated from various sequencing models. Three sequencing models for the hydrolysis are considered: (1) random, (2) block, and (3) random pairs.

Experimental Section

A. Synthesis of Poly(methyl methacrylate). Isotactic PMMA was prepared from the monomer at 0° in toluene solution with phenylmagnesium bromide initiator using the technique described by Goode and his coworkers.[5] Proton resonance spectra, obtained at 90° with a Varian A60 spectrometer, revealed that the polymer contained over 99% isotactic triads as determined by the method of Bovey.[6]

Syndiotactic PMAA was synthesized by irradiating a 20% (by volume) solution of the distilled monomer in dry *n*-propyl alcohol with cobalt 60 γ radiation. The polymerization was performed at $-78°$ with a total dose of 10 Mrad of radiation at a dose rate of 0.4 Mrad/hr. The PMAA was esterified with diazomethane by the procedure of Katchalsky and Eisenberg.[7] The polymer contained 88% syndiotactic triads as determined from nmr spectra of the methylated polymer.

B. Hydrolysis of PMMA. The PMMA samples were freeze dried from benzene to obtain very small particles. Sulfuric acid (100 ml of 97.5%) was placed in a 250-ml flask that was purged continuously with dry nitrogen. About 300-mg of polymer was added to the flask, and the nitrogen purge gas was bubbled vigorously through the acid

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[1] (a) Presented at the 158th National Meeting of the American Chemical Society, New York, N.Y., 1969; (b) submitted in partial fulfillment of the requirements for the degree of Master of Science.

[2] G. Smets and W. E. De Loecker, *J. Polym. Sci.*, **45**, 461 (1960); (b) *ibid.*, **40**, 203 (1959).

[3] K. Matsuzaki, T. Okamoto, A. Ishida, and H. Sobue, *ibid., Part A*, **2**, 1105 (1964).

[4] P. J. Flory, *J. Amer. Chem. Soc.*, **61**, 1518 (1939).

[5] W. E. Goode, F. H. Owens, R. P. Fellmann, W. H. Snyder, and J. E. Moore, *J. Polym. Sci.*, **46**, 317 (1960).

[6] F. A. Bovey and G. V. D. Tiers, *ibid.*, **44**, 173 (1960).

[7] A. Katchalsky and H. Eisenberg, *ibid.*, **6**, 145 (1951).

to provide mixing. After the polymer was dissolved (about 1 min), the flask was placed in a 45° bath for 5–12 min for isotactic PMMA and 1–3 hr for syndiotactic PMMA. The flask was subsequently cooled in an ice bath, and the polymer was precipitated and washed with cold diethyl ether. A small portion of each as-hydrolyzed polymer was examined by ir. The remainder of each sample was refluxed in distilled water for 24 hr to convert any anhydride present to acid.

C. Thermal Formation of Anhydride. The temperature and time interval used in the thermal dehydration process of the copolymers are determined from the dehydration behavior of the isotactic and syndiotactic PMAA homopolymers. Since isotactic PMAA homopolymer is dehydrated to the maximum possible extent in 2 hr at 190°, the isotactic copolymers are dehydrated under these conditions. The dehydration was performed in a dry nitrogen atmosphere to minimize degradation. The weight loss of the samples was also recorded. The syndiotactic polymers were dehydrated in the same manner at 250° to ensure maximum dehydration.

D. Infrared Spectra. All polymer samples were mixed with potassium bromide, ground for 12 min in a vibrating ball mill, and pressed into pellets. Spectra were obtained using a Perkin-Elmer Model 521 spectrometer. The automatic gain control was employed for all compensated spectra.

E. Neutralization of Carboxyl Groups. The copolymers were neutralized with sodium hydroxide by placing finely ground polymer in 1 equiv (assuming 100% hydrolysis) of aqueous sodium hydroxide at 0°. After 20 hr, the polymers were washed with cold 2-propanol. A portion of the washing agent was chilled and placed under vacuum to remove the volatile materials; the residue was subsequently dried under vacuum at 50° and analyzed by ir spectroscopy.

Results and Discussion

A. Composition of Polymers. The degree of hydrolysis, α, and the degree of dehydration, β, are determined by infrared absorption spectroscopy. Spectra of isotactic PMMA and PMAA homopolymers and dehydrated isotactic PMAA are shown in Figure 1. The strong carbonyl stretching bands of the ester (1727 cm^{-1}), acid (1705 cm^{-1}), and anhydride (1800 and 1755 cm^{-1}) are utilized for calculating the polymer compositions. The extinction coefficients of the ester and acid bands are determined from the homopolymers. It is assumed that these extinction coefficients are identical with those of monomer residues in the partially hydrolyzed copolymers; this assumption is verified by techniques described below.

The extinction coefficient of the anhydride band at 1800 cm^{-1} is calculated from the absorbance of the band in dehydrated PMAA assuming that the degree of dehydration is 86% (the theoretical value for random dehydration[4]). This assumption is reasonable, since residual acid groups are observed in the ir spectra for samples heated for 2 hr or longer at 190° with no change occurring in the spectra (Figure 2). The spectra of dehydrated PMAA also indicate that a very great majority of the anhydride is cyclic. The relative intensities of the two anhydride bands and the 45-cm^{-1} difference in frequency are characteristic of a six-membered cyclic anhydride.[8]

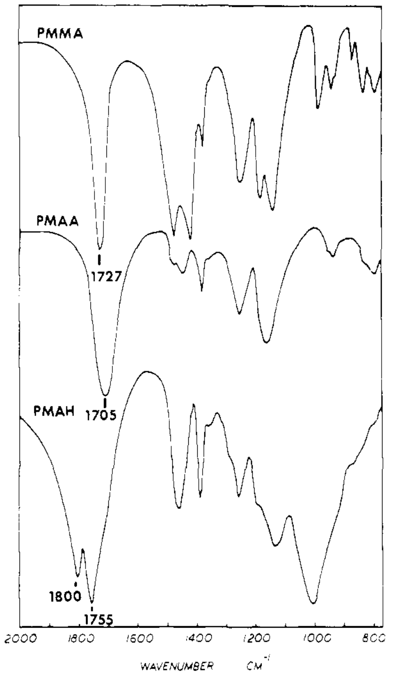
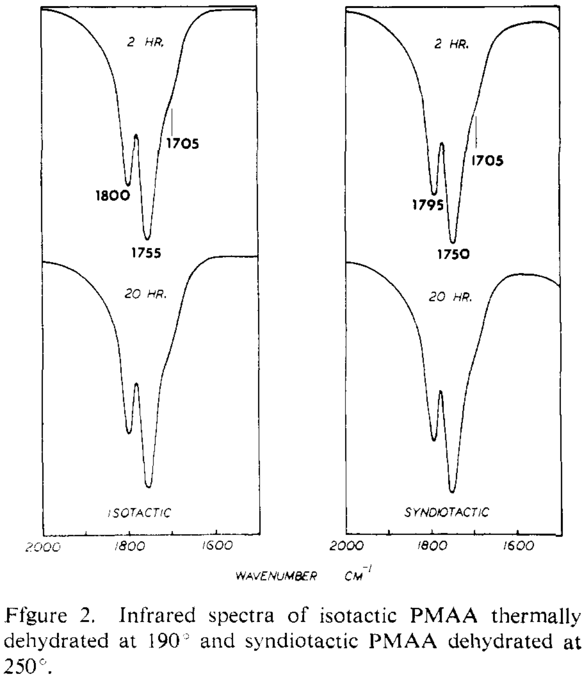


Figure 1. Infrared spectra of isotactic poly(methyl methacrylate) (PMMA), poly(methacrylic acid) (PMAA), and thermally dehydrated PMAA (PMAH).

The degree of hydrolysis in the partially hydrolyzed PMMA copolymers is difficult to determine accurately from spectra of the copolymers, because the acid and ester bands significantly overlap (Figure 3). The degree of hydrolysis is obtained from spectra of copolymers that are neutralized with sodium hydroxide, since the carbonyl oxygen stretching band of the salt (1550 cm^{-1}) is far removed from that of the ester (Figure 3). The degree of hydrolysis is then calculated from the slope of a plot of the absorbance of the 1727 cm^{-1} (ester) band against the total weight of neutralized sample in the potassium bromide pellet.

This technique yields valid degrees of hydrolysis.



Ffgure 2. Infrared spectra of isotactic PMAA thermally dehydrated at 190° and syndiotactic PMAA dehydrated at 250°.

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(8) S. K. Freeman, "Interpretive Spectroscopy," Reinhold Publishing Corp., Inc., New York, N. Y., 1965, p 62.

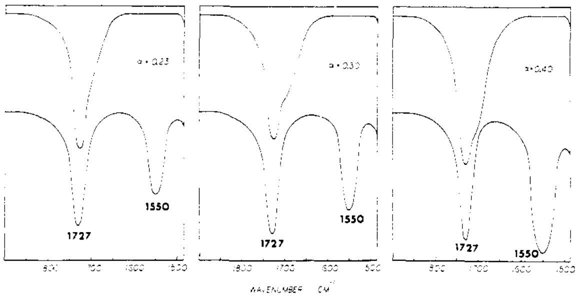

Figure 3. Infrared spectra of partially hydrolyzed isotactic poly(methyl methacrylate) copolymers before (upper spectra) and after (lower spectra) neutralization with sodium hydroxide.

The extinction coefficient of the ester band is insensitive to the presence of the sodium salt; a highly hydrolyzed (thus water-soluble) copolymer had virtually identical values for the degree of hydrolysis determined by both the infrared technique (69.0%) and titration with sodium hydroxide (72.3%). No base-catalyzed hydrolysis of ester groups occurs during neutralization, since PMMA homopolymer treated in the identical manner is not hydrolyzed. In addition, none of the polymer is dissolved in the 2-propanol during washing to remove the excess sodium hydroxide, since the nonvolatile residue obtained by evaporating the 2-propanol is transparent in the infrared carbonyl oxygen stretching region.

The degree of dehydration is also difficult to determine accurately from spectra of the dehydrated copolymers, since the intense ester band obscures much of the carbonyl oxygen region (Figure 4). When the ester band is compensated out by placing an equivalent weight (based on the degree of hydrolysis) of PMMA homopolymer in the reference beam, the degree of dehydration is easily determined from the absorbance of the anhydride (1800 cm^{-1}) and acid bands. The compensated spectra (Figure 4) also show that the acid band has not shifted in frequency.

The experimental degrees of hydrolysis and dehydration for isotactic polymers are summarized in Table I. No corresponding quantities are reported for the syndiotactic polymers, since extensive depolymerization resulted during the dehydration reaction for these samples.

B. Sequence Models and the Expected Degree of Dehydration. Consider a copolymer of methacrylic acid (MAA) and methyl methacrylate (MMA). The maximum conversion of acid to anhydride is a function of both the mole fraction and the distribution of acid monomer units; thus, the per cent anhydride in the heated copolymer can be used to determine the type of sequencing of the monomer units in the original copolymer. We have calculated the expected anhydride content for three hydrolysis sequencing models: (1) random, (2) block, and (3) random pairs. These models are now discussed.

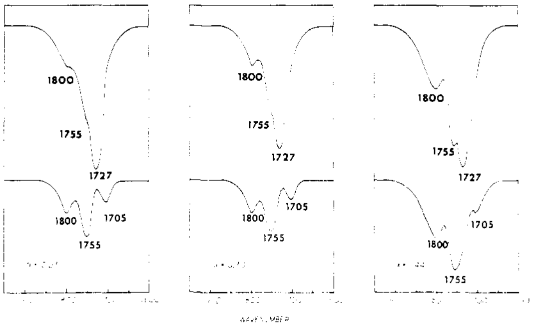

Figure 4. Infrared spectra of partially hydrolyzed isotactic poly(methyl methacrylate) after thermal dehydration (ester band compensated out in lower spectra).

TABLE I
DEHYDRATION OF PARTIALLY HYDROLYZED ISOTACTIC PMMA

Degree of hydrolysis, %	Degree of dehydration, % Exptl	Degree of dehydration, % Random model	z_5,[a] %
23	73	37	96.1
30	79	45	91.7
44	82	58	77.0

[a] z_5 is the per cent of acid groups which would exist as isolated triads (~EAAAE~), diads (~EAAE~), or single units (~EAE~) for random hydrolysis.

1. Random Model. The random sequencing model that is utilized is defined by the following conditions: (1) the hydrolysis of ester groups in PMMA and the dehydration of acid in the copolymer are random processes; (2) only intramolecular anhydride rings are formed by nearest neighbors; (3) the dehydration reaction goes to completion with no adjacent acid monomer units remaining. Consider a sequence of *j* residues in partially hydrolyzed PMMA, *i.e.*

$$\sim EA_1A_2A_3 \cdots A_{j-3}A_{j-2}E\sim$$

where E and A_i are MMA and MAA units, respectively. The fraction of acid, based on all acid monomer units in the copolymer, that occurs in sequences of *j* residues is

$$Z_j = \frac{(j-2)\alpha^{j-2}(1-\alpha)^2}{\alpha} \tag{1}$$

where α is the degree of hydrolysis.

If such a sequence of *j* residues is now dehydrated, the fraction of acid *not* reacted is

$$y_j = Z_j\sum_r\left[\left(1 - \frac{2r}{j-2}\right)M_{j,r}\right] \tag{2}$$

where $M_{j,r}$ is the probability of forming *r* anhydride rings in a sequence of *j* residues. The total fraction *Y* of residual acid units is

$$Y = \sum_{j=3}^{\infty} y_j \tag{3}$$

Equations 1, 2, and 3 are combined to give the final result

$$Y = (1-\alpha)^2\sum_{j=3}^{\infty} C_j\alpha_j^{-3} \tag{4}$$

where

$$C_j = (j-2)\sum_r\left[\left(1 - \frac{2r}{i-2}\right)M_{j,r}\right]$$

The relationship between the anhydride fraction ($1 - Y$) and the degree of hydrolysis is shown in Figure 5.

2. Block Model. In the block model, the acid units of the copolymer all exist in blocks that are long enough (runs of ten or more units) to be treated as homopolymer in calculating the anhydride content; all other assumptions of the random model are retained. Therefore, 86% of the acid is dehydrated for long block sequencing independent of the conversion.

3. Random Pairs Model. Pairs of adjacent ester monomer units are assumed to hydrolyze simultaneously as in hydrolysis directly through the anhydride. The per cent of acid units dehydrated by heating such a copolymer is 100% at low degrees of hydrolysis and approaches 86% with increasing degrees of hydrolysis.

C. Sequencing in the Hydrolysis of Isotactic and Syndiotactic PMMA. Hydrolysis Mechanisms. The experimental anhydride content of the dehydrated isotactic copolymers and that calculated assuming random hydrolysis are compared in Table I. In all samples the experimental value is appreciably larger than that calculated for random hydrolysis and slightly smaller than expected for the block model. Therefore, a strong tendency toward blocking of the acid residues is present. This tendency toward blocking is also confirmed by the behavior of the carbonyl oxygen region of the ir spectra. If the hydrolysis were predominantly random or random in pairs, differences should be observed in the frequency and extinction coefficient of the ester band between spectra of the copolymers and PMMA homopolymer, primarily because hydrogen bonding is expected between the carbonyl oxygen of the ester and its neighboring acid group. However, the compensated spectra of Figure 3 indicate that the ester band is identical in both the copolymers and PMMA homopolymer, which is expected only for a block copolymer. Similar behavior is exhibited by the 1705 cm^{-1} acid band (Figure 6). The difference between the experimental conversion and that expected from a random hydrolysis model cannot be explained by nonrandom dehydration, since in all three copolymers nearly all acid groups would occur in runs of three or less units (see Table I), structures in which the degree of dehydration is independent of the dehydration mechanism, given a random hydrolysis reaction.

The blocking of acid units in partially hydrolyzed isotactic PMMA suggests that ester groups are activated by neighboring hydrolyzed groups. Such neighboring group effects have been previously reported in the base-catalyzed hydrolysis of methacrylate esters[9] and in the hydrolysis of poly(vinyl acetate).[10] The local chain conformation of isotactic PMMA about a hydrolyzed monomer unit is presumably favorable for the hydrolyzed group to activate a neighboring ester group to yield a block copolymer. Morawetz[6] also observed the formation of ring compounds as the hydrolysis product for some methacrylates that were hydrolyzed in the presence of basic catalysts. Thus, it is possible that the hydrolysis of isotactic PMMA in acid solution proceeds through anhydride formation.

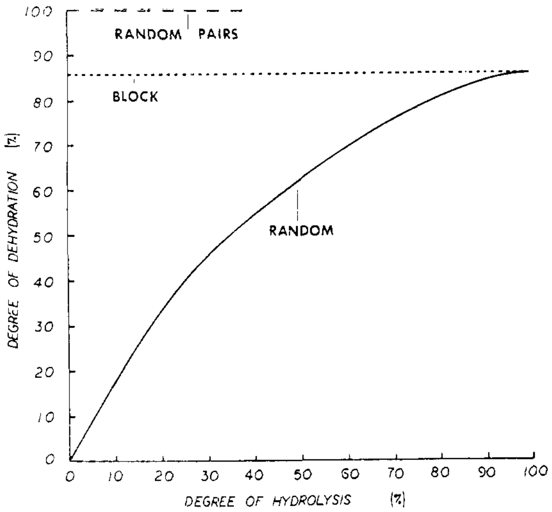

Figure 5. Theoretical degree of dehydration as a function of the degree of hydrolysis for random, block, and random pairs distribution models.

The as-hydrolyzed copolymers of both tacticities contain anhydride rings and free acid as shown by the infrared spectra in Figure 7. The actual fraction of hydrolyzed groups existing as anhydride in sulfuric acid solution cannot be determined from these samples. Some of the anhydride may be lost during precipitation, since thermally dehydrated PMAA homopolymer contains less than 86% anhydride after it is dissolved in sulfuric acid and precipitated (Figure 8). In addition, sulfuric acid is a strong dehydrating agent, and PMAA homopolymer is partially dehydrated when the polymer is dissolved in sulfuric acid and precipitated (Figure 9). Thus, it cannot be established from these observations whether the hydrolysis reactions proceed

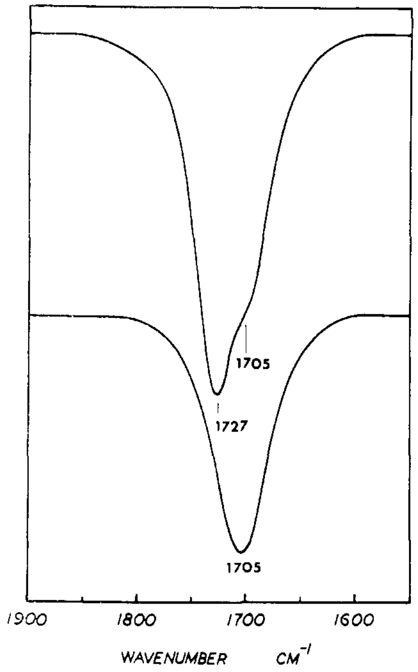

Figure 6. Infrared spectrum of partially hydrolyzed isotactic poly(methyl methacrylate) compensated for the ester band.

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(9) H. Morawetz, *Svensk Kem. Tidskr.*, **79**, 310 (1967).

(10) E. Nagai and N. Sagane, *Kobunshi Kagaku*, **12**, 195 (1955).

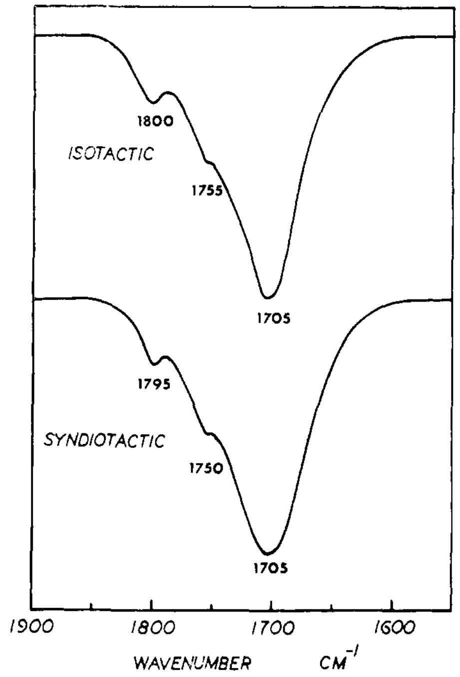

Figure 7. Infrared spectra of as-hydrolyzed PMMA copolymers.

directly through the anhydride; it is equally possible that hydrolysis yields free acid which is subsequently dehydrated by the sulfuric acid.

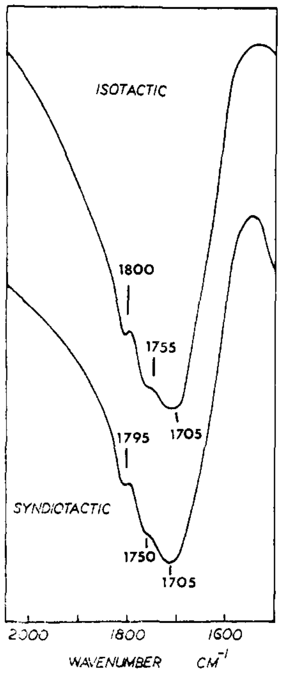

Figure 8. Infrared spectra of dehydrated poly(methacrylic acid) after dissolution in concentrated sulfuric acid.

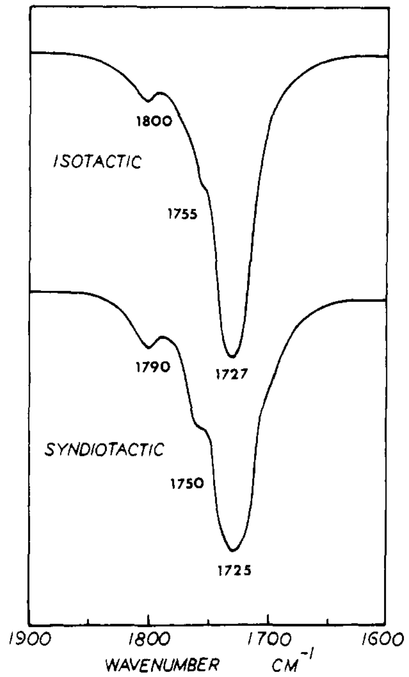

Figure 9. Infrared spectra of poly(methacrylic acid) after dissolution in concentrated sulfuric acid.

The weight loss during the dehydration process was measured for some copolymers, since the technique used to determine the distribution of residues presumes that no depolymerization takes place. The measured weight loss for the isotactic polymers was about twice as large as that calculated from the degree of dehydration determined by the ir technique. Most of this excess weight loss is probably caused by the loss of absorbed water in the polymer prior to heating.[11] Depolymerization and thermal hydrolysis of the isotactic polymers during the dehydration reaction are negligibly small, since the degree of hydrolysis does not change during thermal dehydration. Since the syndiotactic PMMA copolymers depolymerized 30% or more during heating, no determination of the sequencing distribution can be made with the anhydride technique. Depolymerization occurred for the syndiotactic copolymers probably because of the higher temperature required to ensure the maximum extent of dehydration.

Klesper has determined the triad fractions of partially hydrolyzed syndiotactic PMMA samples with 100-MHz proton resonance spectra and has shown that the triad fractions are in good agreement with a random hydrolysis model.[12,13] Thus, the hydrolysis of syndiotactic PMMA cannot proceed directly through the anhydride, and neighboring group effects must be negligibly small.

The striking difference in the distribution of hydrolyzed units in the two stereoregular forms of the copolymers implies that the difference in the maximum extents of hydrolysis has a mechanistic explanation. Suppose that the hydrolysis of the syndiotactic PMMA proceeds randomly in ester units, but when a pentad of the form ~AAEAA~ is produced, the central ester is hydrolyzed at an infinitely slow rate, the rate being slow perhaps because the local chain conformation retards the reaction. The pairs of acid units could presumably be anhydride rings, also. From Monte Carlo experiments, we have determined that the expected conversion is about 81% for this model. The syndiotactic PMMA hydrolyzed to date contain

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(11) V. A. Kargin, V. A. Kabanov, and V. G. Vlasov, *Vysokomol. Soedin.*, 3, 134 (1961).

(12) E. Klesper, *J. Polym. Sci., Part B*, 6, 313 (1968).

(13) E. Klesper, *ibid., Part B*, 6, 663 (1968).

at least 8% heterotactic and isotactic triads, structures which could account for another few per cent hydrolysis required to produce 85% conversion with this model. Besides explaining the observed maximum extent of hydrolysis, this model also predicts triad fractions very nearly equal to those of a purely random process for all degrees of hydrolysis, which is in agreement with the nmr data.[12,13]

The hydrolysis models presented above for the isotactic and syndiotactic polymers are consistent with the relative rates of hydrolysis. If the two polymers are assumed to react at a similar rate at 0% hydrolysis, where both reactions are assumed to be random, the faster reaction of the isotactic polymer can be attributed to the activation of a neighboring ester by each hydrolyzed group.

Kinetic Studies of Anionic Polymerization of Polystyryl Salts in Tetrahydropyran and 2-Methyltetrahydrofuran

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ABSTRACT: Kinetics of homopropagation of the living polystyryl salts were investigated in tetrahydropyran (THP) and 2-methyltetrahydrofuran (MeTHF). Conductance studies of the lithium and sodium polystyryls in THP showed that their dissociation constants, K_d, increase from about 2×10^{-10} *M* at 25° to about 5×10^{-10} and 12×10^{-10} *M*, respectively, at −40°. The relevant propagation constants, k_{obsd}, were determined in THP over a wide concentration range of living polymers, [LE], at 25, 0, −20, and −40° and from the plots k_{obsd} *vs.* $1/[LE]^{1/2}$ the respective values $k_{-}K_d^{1/2}$ were calculated; k_{-} denotes the propagation constant of the free $\sim S^-$ ions. By combining these kinetic data with the conductance findings the values of k_{-} were determined over the investigated temperature range. The linear Arrhenius plot led to $E_{-} = 4.8$ kcal/mol, $A_{-} = 2 \times 10^8$ M^{-1} sec^{-1}, and $k_{-} = 60000$ M^{-1} sec^{-1} at 25°, the values obtained from the studies of the lithium salt being consistent with those derived from the investigation of the sodium salt. It appears, therefore, that the reactivity of the free $\sim S^-$ ions is virtually the same in DME, THF, THP, and THF–dioxane or THF–benzene mixtures. The reactivity of the $\sim S^-,Li^+$ and $\sim S^-,Na^+$ ion pairs in THP is discussed and our results are compared with those obtained by other investigators. The reactivities of the Li^+, Na^+, K^+, and Cs^+ salts of $\sim S^-$ in MeTHF were studied at 25° only. Some undesirable properties of MeTHF are discussed.

Reactions involving ionic species are usually greatly affected by the nature of the solvent. For example, a change from dioxane to dimethoxyethane increases the rate of propagation of polystyrylsodium by a factor of 1000.[1,2] Moreover, the change of solvent may reverse the reactivity order for the polystyryl salts. While in dioxane the propagation rate constant of the polystyryl ion pair increases with the size of the alkali counterion,[1] in tetrahydrofuran[3] and in dimethoxyethane[2] the cesium ion pairs are much less reactive than the lithium and sodium ion pairs.

The understanding of these effects calls for systematic studies of the properties of ethereal solvents, their ability to dissociate ion pairs and to solvate ionic species. Much information on this problem may be obtained from the kinetic studies of anionic polymerization.

Kinetics of homopolymerization of polystyryl salts in dioxane,[1] tetrahydrofuran,[3,4] and dimethoxyethane[2] have been reported recently, and the physical properties of these solvents are described in ref 5. Here we report our findings concerned with anionic propagation of living polystyrenes possessing Li^+, Na^+, K^+, and Cs^+ counterions in methyltetrahydrofuran and tetrahydropyran.

Experimental Section

Commercial 2-MeTHF or THP (Aldrich Chemicals) was refluxed overnight on Na-K alloy, then fractionated and the middle fraction was distilled into the flask containing Na-K alloy and small amounts of benzophenone. The solvent, whenever needed, was redistilled under high vacuum into the required containers.

The one-ended $\sim S^-,Li^+$ was prepared at 0° by adding a styrene solution in MeTHF or THP to the commercial ethyllithium (Foot Co.) freshly purified by repeated crystallization from benzene. The reaction was over in about 0.5 hr and thereafter the aliquots were stored at −78° to avoid any decomposition. All the subsequent manipulations were rapidly performed at low temperatures, and eventually the required solution was brought up to the desired temperature just prior to the kinetic run. The runs lasted a few minutes for [LE] $\sim 10^{-3}$ *M*, and at higher dilution, [LE] $\sim 10^{-5}$ *M*, the conversion exceeded 90% in 1 hr.

Two types of sodium salts of living polystyrene were investigated. The one-ended $\sim S^-,Na^+$ was prepared in

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(1) D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 624 (1965).

(2) T. Shimomura, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **89**, 5743 (1967).

(3) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

(4) T. Shimomura, K. J. Tölle, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **89**, 796 (1967).

(5) C. Carvajal, K. J. Tölle, J. Smid, and M. Szwarc, *ibid.*, **87**, 5548 (1965).