A Novel Method for Preparing Poly(alkyl Methacrylates) and Poly(methacrylic Acids) of Varying Tacticity

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Synopsis

In order to synthesize poly(methacrylic acid) and poly(alkyl methacrylates) over a wide range of polymer tacticity, the anionic polymerization of the following alkyl methacrylates (ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, isobutyl, *tert*-butyl, *n*-amyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-lauryl, and *n*-octadecyl) in toluene using phenylmagnesium bromide initiation was studied. It was found that the amount of isotactic polymer structure generally decreased as the size of the ester group increased. In all cases, the polymers had greater than 50% isotactic triad structure. Whether the polymerization was carried out at 0° or −78°C had little or no effect on the tacticity of the polymer produced. It was found that the poly(alkyl methacrylates) produced could be hydrolyzed in concentrated sulfuric acid to poly(methacrylic acid). The poly(methacrylic acid) produced in the hydrolysis could be esterified with diazomethane to give poly(methyl methacrylate) or with diazoethane to give poly(ethyl methacrylate) with the same tacticity as the poly(alkyl methacrylate) from which the poly(methacrylic acid) was derived. It is possible, therefore, to produce poly(alkyl methacrylates) of a desired tacticity by polymerizing the appropriate monomer, hydrolyzing, and reesterifying the resultant poly(methacrylic acid) with a diazoalkane to give the desired poly(alkyl methacrylate).

INTRODUCTION

This work was begun in an effort to find a convenient synthesis for poly-(methacrylic acids) of various tacticities. Poly(methacrylic acid) can be prepared from poly(methyl methacrylate) by hydrolysis as well as directly from methacrylic acid. Because of the acidic proton on methacrylic acid, many initiators, for example, metal alkyls, used for the production of stereoregular polymers cannot be used to make poly(methacrylic acid) directly. Stereoregular polymers of methacrylic acid esters have been produced using organometallic initiators, however, and the hydrolysis of these esters provides a convenient synthesis of stereoregular poly(methacrylic acid).

Methyl methacrylate is the most commonly polymerized ester of methacrylic acid, and both isotactic and syndiotactic poly(methyl methacrylate) have been prepared. It is possible to produce polymers of methyl meth-

acrylate which have tacticities between isotactic and syndiotactic by use of appropriate solvents using anionic polymerization. This empirical method of varying tacticity is very difficult to control and the polymers produced consist of long blocks of isotactic and syndiotactic structure rather than a homogeneous polymer structure. It was hoped that this work would provide an easily controllable method of varying the tacticity of poly(methacrylic acid) the stereochemical composition of which would be fairly homogeneous.

RESULTS AND DISCUSSION

As the introduction states, one of the objectives of the research reported in this publication was to find a convenient synthesis of poly(methyl methacrylate) and poly(methacrylic acid) over a broad range of tacticity. This objective might be reached by the anionic polymerization of alkyl methacrylates having ester groups of varying size and steric requirements. In toluene, using phenylmagnesium bromide initiation, an isotactic polymer is formed if the alkyl ester group is small (for example, methyl). If alkyl methacrylates with more bulky ester groups were polymerized under these same conditions, polymers with less isotactic structure should result because steric interaction should decrease the probability of isotactic addition to the growing polymer chain. Poly(methacrylic acid) could be obtained from the poly(alkyl methacrylates) by hydrolysis without changing the tacticity of the polymer. Furthermore, reesterification of the poly(methacrylic acid) with diazomethane would result in poly(methyl methacrylate) of the same tacticity as the original poly(alkyl methacrylate).

The literature contains many reports relevant to the anionic polymerization of alkyl methacrylates.[1-21] Until this time, no one has made a systematic study of the effect of the steric requirements of the ester group on the tacticity of anionically polymerized poly(alkyl methacrylates). While the literature does contain scattered information on a considerable number of anionically produced poly(alkyl methacrylates), the comparison and interpretation of these results is impossible because only a few of the polymerizations have been carried out under identical conditions. One, therefore, cannot decide whether differences in the stereochemistry are a result of the change in monomer or some other variable in the system such as initiator, solvent, temperature, concentration, or polymerization time. This is the first study to include such a large number of monomers polymerized under essentially the same conditions. The following monomers have been polymerized at 0° and −78°C: ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, sec-butyl methacrylate, isobutyl methacrylate, n-amyl methacrylate, n-hexyl methacrylate, n-octyl methacrylate, and n-decyl methacrylate. In addition, tert-butyl methacrylate, n-lauryl methacrylate and n-octadecyl methacrylate were polymerized at 0°. To our knowledge, the anionic polymerization of the following monomers has not been reported in the literature: n-amyl methacry-

late, n-hexyl methacrylate, n-octyl methacrylate, n-decyl methacrylate, n-lauryl methacrylate, and n-octadecyl methacrylate.

The polymerizations were carried out using toluene as the solvent and an ethereal solution of phenylmagnesium bromide as the initiator. This combination of solvent and initiator leads to an isotactic polymer if the monomer is methyl methacrylate.[3] The ether associated with the Grignard reagent could be a complicating factor in the polymerization since it constitutes about 1% of the reaction mixture. Glusker and co-workers[22] have shown, however, that small amounts of ether do not noticeably affect the polymerization of methyl methacrylate.

Since there is no general procedure available for the facile examination of the stereochemistry of most of the poly(alkyl methacrylates), it was necessary to transform the polymers in some fashion to make information concerning the stereochemistry more accessible. It was decided that the most feasible procedure would be to hydrolyze the polymers to make poly-(methacrylic acid), then esterify this polymer to poly(methyl methacrylate). Poly(methyl methacrylate) has been studied in great detail, and there are several methods available for determining its tacticity. The hydrolysis of the poly(alkyl methacrylates) to poly(methacrylic acid) was performed in concentrated sulfuric acid.[23,24] Diazomethane was generated by the procedure given by Arndt,[25] and the poly(methacrylic acid) samples were esterified with diazomethane according to the procedures given by Katchalsky and Eisenberg[23] and Jellinek and Lipovac.[24]

After hydrolysis and reesterification of the polymers to yield poly-(methyl methacrylate), the tacticity of the polymers could be determined. Two methods were used to determine the tacticity of the poly(methyl methacrylate) samples derived from the poly(alkyl methacrylates). One was an infrared method described by Goode and his co-workers.[3] The determination of small differences in stereochemistry by this method is very difficult. The J values of several polymers are given in Table I.

The second method used for determining the tacticity of the polymers made use of nuclear magnetic resonance (NMR). Bovey and Tiers[7] were the first to make use of NMR to determine the tacticity of poly(methyl methacrylate), and they took their spectra from polymers dissolved in chloroform in sealed tubes at 90°C. In this work, chloroform was used as a solvent at 37°C. It was noted, however, that resolution could be improved by taking the spectra in o-dichlorobenzene at elevated temperatures, a system suggested by Ramey.[26] The spectra were taken in this solvent at 148°C. The spectra taken from the polymers in o-dichlorobenzene retained the essential features of the spectra taken in chloroform, but the peaks were shifted. The peaks due to the α-methyl group protons in the isotactic, heterotactic, and syndiotactic triads were respectively shifted to $\delta = 1.14$, 1.03, and 0.91 ppm, the center of the methylene proton absorption was shifted to $\delta = 1.88$ ppm, and ester proton absorption was shifted to $\delta = 3.59$ ppm.

There was a considerable disparity between tacticity found in o-dichloro-

TABLE I

Comparison of Tacticity of Various Poly(methyl Methacrylates) Prepared From Poly(alkyl Methacrylates) Found by Infrared and Nuclear Magnetic Resonance Analyses[a]

Parent poly(alkyl methacrylate)	Polymerization temp., °C	o-Dichlorobenzene[b]				Chloroform[b]		
		J	$i, \%$	$h, \%$	$s, \%$	$i, \%$	$h, \%$	$s, \%$
Ethyl	0	35	90	8	3	79	12	8
	−78	32	91	7	3	77	15	8
n-Propyl	0	34	88	9	3	—	—	—
	−78	32	86	7	7	—	—	—
Isopropyl	0	27	83	12	6	69	18	6
	−78	32	83	10	7	78	13	9
n-Butyl	0	32	83	6	11	71	15	14
	−78	22	80	11	10	73	16	11
sec-Butyl	0	32	78	13	9	65	16	19
	−78	32	81	9	10	68	19	14
Isobutyl	0	—	81	9	10	65	20	16
	−78	—	78	12	10	69	15	15
tert-Butyl	0	32	57	27	16	—	—	—
n-Amyl	0	35	79	10	11	64	19	17
	−78	28	84	8	8	63	21	17
n-Hexyl	0	38	81	9	10	60	21	19
	−78	35	84	9	7	68	18	14
n-Octyl	0	29	80	11	9	68	16	15
	−78	29	77	10	13	57	22	22
n-Decyl	0	30	75	15	10	58	20	22
	−78	33	73	13	13	—	—	—
n-Lauryl	0	26	72	13	15	—	—	—
n-Octadecyl	0	30	69	15	15	59	19	22

[a] J = Infrared value relevant to polymer tacticity[3]: where J = 25–35, polymer is isotactic; where $J > 100$, polymer is syndiotactic; where $J > 35$ and < 100, polymer is atactic. i = Isotactic triads; h = heterotactic triads; s = syndiotactic triads.
[b] NMR solvent.

benzene and chloroform (see Table I). This is in part due to the lower resolution obtained in the latter solvent. Regardless of which solvent the spectra were taken in, the conclusions reached are the same.

As can be seen from the results obtained in o-dichlorobenzene, the percentage of isotactic triads gradually decreases as the length of the n-alkyl group is increased. Branching has only a small effect on the isotacticity, except for tert-butyl methacrylate. This polymer gave rise to the lowest degree of isotacticity observed for any of the polymers. While the isotactic character of the polymers decreased with increasing bulk of the ester group, this decrease is not as great as was expected.

Comparison of the results obtained in these studies with other results in the literature is complicated by differences in the experimental procedures used to produce the polymers and to evaluate the tacticity. None the less, these results are in general agreement with other results in the literature.[10–21]

Since poly(methyl methacrylate) can be obtained from poly(methacrylic acid) by reaction with diazomethane, it seemed probable that reaction of poly(methacrylic acid) with other alkyl diazo compounds could provide a useful synthetic method for the preparation of poly(alkyl methacrylates) of varying tacticity. Accordingly, diazoethane was prepared by standard techniques and reacted with a sample of poly(methacrylic acid) prepared by anionic polymerization of ethyl methacrylate (see Tables I and II) and subsequent hydrolysis to the acid. The poly(ethyl methacrylate) formed by reesterification with diazoethane was identical in all respects (including tacticity) with the sample of poly(ethyl methacrylate) from which it was derived. Thus, it would appear that poly(alkyl methacrylates) of various tacticities can be prepared using the principles and techniques described herein, provided that the needed diazoalkane is available.

TABLE II
Data Concerning the Preparation and Properties of
Various Poly(alkyl Methacrylates)

Ester	Polymerization temp., °C	Polymer yield, %	Intrinsic viscosity, dl/g	Melting point, °C
Ethyl	0	45	0.47	70–75
Ethyl	−78	89	0.20	60–70
n-Propyl	0	44	0.39	45–50
n-Propyl	−78	59	0.38	45–50
Isopropyl	0	93	1.00	89–90
Isopropyl	−78	56	0.68	129–130
n-Butyl	0	40	0.24	40–50
n-Butyl	−78	52	0.45	75–85
sec-Butyl	0	92	0.47	70–80
sec-Butyl	−78	92	0.26	70–80
Isobutyl	0	45	0.53	60–75
Isobutyl	−78	89	0.43	65–75
tert-Butyl	0	80	0.08	65–75
n-Amyl	0	93	0.15	25–50
n-Amyl	−78	89	0.34	tacky at 25
n-Hexyl	0	70	0.10	tacky at 25
n-Hexyl	−78	45	0.26	tacky at 25
n-Octyl	0	58	0.44	tacky at 25
n-Octyl	−78	96	0.16	tacky at 25
n-Decyl	0	35	0.31	tacky at 25
n-Decyl	−78	45	0.20	tacky at 25
n-Lauryl	0	58	0.10	tacky at 25
n-Octadecyl	0	83	0.15	40–45

EXPERIMENTAL

Monomers were purchased from the Borden Co. (Monomer-Polymer Laboratories). Monomers were washed with 10% aq. NaOH, dried with $MgSO_4$, and distilled at reduced pressure before use. Melting points were taken on a hot stage.

Two typical polymerization experiments are described below, and the remainder of the polymerization experiments are summarized in Table II.

Polymerization of Ethyl Methacrylate 0°C. Fifty milliliters of distilled, dried (sodium metal) toluene (Fisher reagent) was redistilled into a serum bottle of ca. 100-ml capacity. A large porcelain plate boiling chip was suspended in the toluene by a fine wire. The toluene in the serum bottle was brought to a vigorous reflux and boiled until vapors emanated from the neck of the bottle. The heating mantle was removed from under the serum bottle, then the wire and boiling chip were removed. The bottle was stoppered quickly with a serum bottle cap. A hypodermic needle attached to a line supplying nitrogen was inserted through the serum bottle cap. The nitrogen admitted to the serum bottle was made oxygen free by bubbling through an alkaline solution of pyrogallol, then dried by passing through a trap containing anhydrous magnesium sulfate and a 1-m column of silica gel. The serum bottle was immersed in an ice bath in a Dewar flask for 15 min. The hypodermic needle admitting nitrogen to the serum bottle was withdrawn, and the bottle was momentarily removed from the ice bath. With a 1-ml syringe, 0.4 ml (0.72 meq) phenylmagnesium bromide solution containing 1.79 meq/ml phenylmagnesium bromide in ether was added to the toluene. The addition of the initiator was quickly followed by the addition of 3.0 ml (2.7 g) ethyl methacrylate by means of a 10-ml syringe. The ethyl methacrylate had previously been distilled and collected at 121°–22°C. The reaction vessel was placed back in the ice bath, and the polymerization was allowed to continue for 20 hr. The polymerization was terminated by adding 2 ml methanol to the viscous solution and shaking vigorously. The polymerization mixture was poured into a 250-ml round-bottom flask and evaporated to dryness using a rotating evaporator. The flask from which evaporation was taking place was warmed by a water bath the temperature of which was not greater than 50°C. After the contents of the flask had reached dryness, the flask was removed from the rotating evaporator and the solid material was extracted with two 20-ml portions of methanol. The methanol was decanted leaving the polymer, which was dissolved in 30 ml benzene. The benzene solution was placed in a beaker containing 100 ml water, and the benzene was evaporated on a steam bath. The water was decanted, and the polymer was dried in an oven at 100°C. The polymer, which adhered to the sides of the beaker, was dissolved in a few milliliters of benzene which was poured into a weighted sample bottle and evaporated to dryness under vacuum. The yield was 1.2 g (45%) translucent white polymer melting at 70°–75°C.

Polymerization of Ethyl Methacrylate at −78°C. Fifty milliliters of distilled, dried (sodium metal) toluene (Fisher reagent) was redistilled into a serum bottle of about 100-ml capacity, stoppered with a serum cap, and flushed with nitrogen gas as described above. The serum bottle was cooled in an ice–salt bath for several minutes, then placed in a Dry Ice–acetone bath in a Dewar flask. The bottle was shaken slightly at short

intervals until bubbles of carbon dioxide no longer rose from around the bottle (about 10 min). The bottle was removed from the Dry Ice-acetone bath, and the hypodermic needle admitting nitrogen was removed. By means of a 1-ml syringe, 0.4 ml (0.92 meq) phenylmagnesium bromide solution containing 2.30 meq/ml phenylmagnesium bromide in ether was added to the toluene. The addition of the initiator was quickly followed by the addition of 3.0 ml (2.7 g) ethyl methacrylate by means of a 10-ml syringe. The ethyl methacrylate had previously been distilled and collected at 121°–122°C. The reaction vessel was returned to the Dry Ice-acetone bath. The Dewar flask was stoppered with a large rubber stopper with a small hole in the middle. The Dewar flask was placed in the freezer at −20°C, and the polymerization was allowed to continue for 26 hr. The reaction vessel was removed from the Dry Ice–acetone bath, and 2 ml methanol was added through the serum cap. The bottle was shaken and allowed to warm in a bath containing warm water. The polymerization mixture was poured into a 250-ml round-bottom flask and evaporated on a rotating evaporator. The flask from which evaporation was taking place was warmed by a water bath the temperature of which was not greater than 50°C. The contents of the flask were taken to complete dryness by means of a high-vacuum pump attached to the rotating evaporator. The polymer was dissolved in benzene which was poured into a weighted sample bottle and evaporated to dryness under vacuum. The yield was 2.5 g (89%) translucent white polymer melting at 60–70°C.

Viscosity Measurements. The intrinsic viscosities of the polymers were obtained in the usual manner. The viscosity data is shown in Table II.

Hydrolysis of Poly(alkyl Methacrylates).[23,24] The hydrolysis of the poly(alkyl methacrylates) was carried out by adding 50 ml 96% sulfuric acid to a weighed amount of polymer (ca. 0.5 g) and stirring the reaction mixture with a magnetic stirrer in a covered beaker for two days, with the following exceptions: The poly(sec-butyl methacrylate) prepared at −78°C was hydrolyzed for three days, the poly(n-hexyl methacrylate) prepared at −78°C was hydrolyzed for six days, and poly(n-decyl methacrylate) was hydrolyzed for seven days. During the hydrolysis, the reaction mixtures turned yellow, then brown. The darkness of the solutions increased with increasing length of the alkyl ester group. The poly(n-lauryl methacrylate) and poly(n-octadecyl methacrylate) polymers gave almost black reaction mixtures. After hydrolysis, the reaction mixtures were poured (with vigorous stirring) into a 250-ml beaker filled with crushed ice. The polymer was filtered off and the still moist polymer was dissolved in 20 ml of either dimethylformamide or methanol, this solution of the polymer was poured into 200 ml dilute aqueous hydrochloric acid, and the precipitated colorless polymer was filtered. The poly(methacrylic acid) was dried in air, then under vacuum.

Esterification of Poly(methacrylic Acids) with Diazomethane.[23,24] The poly(methacrylic acids) from the hydrolysis of the poly(alkyl methacrylates) were esterified with diazomethane to yield poly(methyl meth-

acrylate) by the following procedure. The poly(methacrylic acid) was suspended in 50 ml benzene in a beaker. Diazomethane in ether solution was distilled into the reaction mixture. Vigorous bubbling took place, and the reaction was allowed to continue for 24 hr or until the yellow color of diazomethane was discharged. The solution or suspension was then evaporated on the steam bath to a few milliliters, and benzene was added to bring the volume back to 50 ml. More diazomethane was distilled into the benzene–polymer mixture. If after 1 hr no bubbles formed, the polymer solution was evaporated to dryness on the steam bath. If bubbles did rise, the reaction was left for 24 hr, the solvent was evaporated to a small volume on the steam bath, and then the volume was brought back to 50 ml by the addition of benzene. More diazomethane was distilled into the polymer–benzene mixture. If any bubbles rose during the first hour, the mixture was left standing overnight, otherwise the mixture was evaporated to dryness. If the reaction mixture had been left standing overnight, the color of the excess diazomethane was still present, and these solutions also were evaporated to dryness to isolate the polymer.

A further complication during the hydrolysis and reesterification of the polymers was the formation of what appeared to be a carboxylic acid anhydride. There is in the infrared spectrum of the reesterified polymer a band at 1800 cm^{-1} which can be ascribed to the carboxylic acid anhydride. Sobue, Matsuzaki, and Nakano[27] also noted this band and decided that it was due to a small amount of anhydride in the polymer because of the wavelength of the infrared absorption and because the function causing the band could be removed by boiling the polymer in water. In our work, the band also could be removed (via esterification) by boiling the polymer with a solution of methanol, benzene, and a few drops of concentrated sulfuric acid. Whenever the band was noted in the infrared spectrum of a reesterified polymer, it was removed by this procedure. The anhydride did not form all of the time, and the formation was probably governed by the efficiency of sulfuric acid removal from the hydrolysis product and the conditions under which the polymer was dried. Anhydride formation did not occur if the polymer was air dried at room temperature.

Esterification of Poly(methacrylic Acid) with Diazoethane. A solution of 0.15 g isotactic poly(methacrylic acid) [prepared by hydrolysis of poly-(ethyl methacrylate)] in 50 ml dimethylformamide was made. The diazoethane–ether solution was added, and the reaction was allowed to proceed with stirring overnight. Vigorous evolution of bubbles took place, and by morning the yellow color of the solution had disappeared. Another diazoethane–ether solution was added. Mild evolution of nitrogen ensued. After 3 hr no more bubbles rose and the solution was still yellow. The solution was heated on the steam bath and dried under a stream of nitrogen. The nuclear magnetic resonance spectrum of the clear, white polymer was identical with that of the poly(ethyl methacrylate) from which it was derived.

Nuclear Magnetic Resonance Spectra. The nuclear magnetic resonance spectra of the poly(methyl methacrylates) derived from the poly(alkyl methacrylates) were taken on a Varian Associates A60-A nuclear magnetic resonance spectrometer. The polymers were weighed and dissolved in enough o-dichlorobenzene (distilled b_{760} = 180°–183°C) to give a 10–15% solution. The solutions were placed in the NMR sample tube, and the spectra were run at 148°C using the variable temperature probe of the NMR spectrometer. The temperature of the thermostat was checked periodically by noting the number of cycles between the two peaks of an ethylene glycol sample. The temperature was calculated from the difference in the chemical shifts of the two peaks using a calibration curve supplied by Varian Associates.

The percentage of isotactic, syndiotactic, and heterotactic triads was calculated from the NMR spectrum in the following way. The spectrum of a sample of atactic poly(methyl methacrylate) was used as a reference for decomposing the peaks due to the α-methyl protons into the three peaks corresponding to the three triads. A baseline was drawn from about 3.0 ppm δ to 0 ppm δ. The spectrum was placed over the spectrum of the reference sample, and the peaks due to the isotactic triads were aligned. Vertical lines were then dropped from the points on the curve representing minimums between peaks in the reference spectrum to the baseline. Because of the low percentage of heterotactic and syndiotactic triads in most of the polymers, the peaks due to these protons were not clearly resolved and the use of the reference sample was necessitated. The areas under the three peaks due to the α-methyl protons in the three different triads were found by using a plainmeter, and the percentage which each contributed to the total area was calculated.

The spectra of many of the polymers also were taken in chloroform at 37°C. The ethyl alcohol used as a stabilizer in the chloroform was removed by reacting 125 ml chloroform with 3 g phosphorous pentoxide for 1 hr, filtering off the solid material, and distilling the chloroform. The fraction boiling at 65.5° ± 0.5°C was collected. The area under each of the α-methyl peaks was found in a similar manner. A comparison of the results in o-dichlorobenzene and chloroform is given in Table I. The resolution of the spectra taken in chloroform was much lower, and so the results taken in o-dichlorobenzene are more accurate.

Infrared Spectra. The infrared spectra of the poly(methyl methacrylates) and the poly(alkyl methacrylates) were recorded on a Perkin-Elmer Model 237 infrared spectrometer. The spectra of thin films of the polymer cast from a benzene solution onto a potassium bromide pellet were taken. The J values were calculated by the method given by Goode and co-workers.[3] The J values of some poly(methyl methacrylate) samples are given in Table I with the percentages of isotactic, heterotactic, and syndiotactic triads found by NMR. The results show the inadequacy of the infrared method under these circumstances.

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