

The Preparation of Block Copolymers of Styrene and Methacrylic Acid

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Synopsis

A new method of preparing block copolymers of styrene and methacrylic acid is described. It is based upon use of the anionically initiated "living chain" method to prepare block copolymers of styrene and methyl methacrylate, with subsequent hydrolysis of the methyl methacrylate block to methacrylic acid.

INTRODUCTION

Two methods have hitherto been available for the preparation of block copolymers of styrene and methacrylic acid. In the suspension method^{1,2} a growing polymer chain migrates across a phase boundary into another monomer where growth continues. Application of the method to the present cases involves dispersion of styrene droplets in an aqueous solution of methacrylic acid, containing also water-soluble initiator and suspension stabilizer, at a temperature sufficient to decompose the initiator.

The alternative method¹ is to irradiate, in the presence of a second monomer, a polymer possessing photochemically active endgroups. Thus, the polymerization of styrene in the presence of carbon tetrabromide results, by means of chain transfer, in the formation of polystyrene with bromine endgroups. Subsequent photolysis of this polystyrene in the presence of methacrylic acid leads to the block copolymer.

These methods possess certain disadvantages. The copolymers are normally contaminated with one or both of the homopolymers (indeed, the copolymer may even be a minor constituent), and a separation process is required. In addition, it is difficult to make block copolymer of predetermined composition, and a rather tedious "trial and error" approach may be needed. The molecular dispersity is also high, as shown by the exceptionally broad GPC traces shown by polymers prepared in this way. The first method gives polymers in which the blocks are not homopolymeric, a situation resulting from the mutual solubility of the two monomers.

A versatile method³ of making block copolymer, which is largely free from these disadvantages, is the anionic "living chain" method. Using this method, block copolymers possessing narrow molecular weight distributions and of uniform composition have been obtained in good yield. How-

ever, the method is not directly applicable to systems involving methacrylic acid since any proton-donating material will "kill" the "living chains." It was proposed, therefore, to apply the method to the styrene-methyl methacrylate system and to hydrolyze the methyl methacrylate units in a subsequent stage.

A difficulty with this procedure is that hydrolysis of poly(methyl methacrylate) does not always proceed to completion. The hydrolysis of atactic poly(methyl methacrylate) has been observed⁴ to proceed to about 85% conversion. Similarly, the limiting extent of hydrolysis, under acid conditions, of syndiotactic poly(methyl methacrylate) was also found⁵ to be 85%. In contrast, isotactic polymer hydrolyzed completely in a relatively short time. It was hoped, therefore, that by preparing the methyl methacrylate blocks under conditions such that they might be expected to be isotactic, they would be amenable to complete hydrolysis. Such conditions are provided by anionic polymerization in a hydrocarbon solvent at -60°C .⁶

EXPERIMENTAL

Preparation and Purification of Materials

Toluene. The toluene was refluxed with molten sodium for 7 hr and then distilled. The middle fraction was collected over calcium hydride, over which it was stored until required.

Monomers. Styrene and methyl methacrylate were distilled under vacuum. The middle fractions were retained and stored, over calcium hydride, in a refrigerator.

***n*-Butyllithium.** A 22.0 wt-% solution in hexane, as supplied by Alpha Inorganics Inc., was used.

Nitrogen. British Oxygen Company "White Spot" nitrogen was dried by passing through a column of a molecular sieve and then bubbled through a flask containing a solution of "living" polystyrene in toluene.

Preparation of Copolymers

A 250-ml Buchner flask, containing a magnetic stirrer chaser, was fitted with a Subaseal and placed in an oven at 100°C for 15 min to remove moisture. It was then evacuated with the aid of an oil pump and placed in a water bath over a magnetic stirrer/hot plate. The water bath was maintained at 50°C . The tap between the flask and the vacuum pump was closed, and dried nitrogen was admitted through the Subaseal with the aid of a hypodermic syringe barrel and needle.

Toluene (100 ml) was syringed into the flask; and when the nitrogen pressure in the flask was slightly greater than atmospheric, the tap was opened to the atmosphere. Nitrogen was passed through the flask at a steady rate, and the stirrer was switched on. Styrene, 1 ml, was syringed into the flask, followed by 5 ml of the *n*-butyllithium. The remainder of the styrene was then added.

The contents of the flask were stirred at 50°C for 1 hr, after which the water bath was replaced by a solid CO₂/acetone bath. After 15 min, the contents of the flask had assumed the temperature of the bath, and the methyl methacrylate was added via syringe. The red color, characteristic of polystyrene anions, disappeared, and after about 30 min the viscosity of the solution had noticeably increased. After a further 30 min, the copolymer was precipitated by addition to methanol, filtered off, and dried in the air and then in a vacuum oven, at 60°C for 18 hr.

A range of copolymers was prepared in this way, by varying the amounts of the two monomers used. The polymers formed were examined for purity by gel permeation chromatography and by fractional precipitation, followed by spectroscopic analysis of the fractions. Most of the copolymers were homogeneous, giving a single GPC peak and being separated by fractionation into fractions differing only in molecular weight. A few of the copolymers, notably those with low styrene content, showed double peaks on the GPC trace. Presumably, poly(methyl methacrylate) is formed concurrently with the copolymer as the result of *n*-butyllithium carrying through to the second stage and/or by termination of polystyryl anions by methyl methacrylate followed by homopolymerization of the latter. In these cases, separation was achieved by fractional precipitation by methanol from tetrahydrofuran. The fractions obtained showed a single peak on the gel permeation chromatograph.

Hydrolysis of the Copolymers

The copolymer (1.5 g) was dissolved in a mixture of acetic acid (100 g) and toluene-*p*-sulfonic acid (3 g). The solution was raised to reflux and a few drops of water were added, care being taken not to precipitate any polymer. In those cases where the styrene content of the polymer was greater than 80%, dimethylformamide (up to 20 ml, depending on the polymer) was added to the refluxing mixture in order to effect solution. Reflux was maintained for one week. The product was precipitated by addition to water (1 liter), filtered off and washed with a large volume of water. It was dried in a vacuum oven overnight at 60°C. The product was then dissolved in dimethylformamide, reprecipitated by addition of water, filtered, and dried overnight in a vacuum oven at 60°C. Final drying was achieved by dissolving in benzene and freeze drying.

Analysis of the Copolymers

The compositions of the block copolymers of styrene and methyl methacrylate were determined by the method of Unwin and Stearne,⁷ which involved measurement of the optical density of the copolymers in chloroform at 262 μ . The specific extinction coefficient of the copolymer is assumed to be linearly related to the specific extinction coefficients of the two homopolymers and to its weight fraction composition.

In addition, composition was determined by measurement of refractive index increment, as described by Bushuk and Benoit.⁸ Again, the refractive index increment of the copolymer is assumed to be simply related to the values for the homopolymers and the composition of the copolymer.

The degree of hydrolysis of the hydrolyzed copolymers cannot be reliably obtained by direct application of IR spectroscopy because there is significant overlap of the acid and ester bands. However, this difficulty can be overcome⁹ by neutralizing the acid groups with sodium hydroxide. The carbonyl oxygen stretching band of the carboxylate ion (1550 cm^{-1}) is far removed from that of the ester (1727 cm^{-1}). The copolymers were neutralized by an equivalent amount of sodium hydroxide. The neutralized polymer was obtained by evaporation and incorporated into KBr discs. The spectrum was obtained using a Unicam SP200 spectrometer. Absence of peaks at 1727 cm^{-1} indicated complete hydrolysis.

Confirmation of this was obtained by aqueous titration. About 0.05 g hydrolyzed polymer was weighed accurately into a 100-ml beaker, and 25 ml 0.1M sodium hydroxide solution was added by means of a pipet. The mixture was warmed at ca. 40°C for 1 hr, during which time the polymer dissolved. The residual base was determined potentiometrically, using standard 0.1M hydrochloric acid with an E.I.L. Model 23A direct-reading pH meter. Readings were taken on the millivolt scale. The mole-% methacrylic units were calculated on the assumption that hydrolysis was complete.

RESULTS AND DISCUSSION

Polymer Preparation

A series of block copolymers of styrene and methyl methacrylate was prepared by the method described above. Conditions were such that the methyl methacrylate blocks might be expected to be largely isotactic and the whole composition range was covered. Details of the polymers prepared are given in Table I. The compositions of the polymers, as determined by the ultraviolet and refractive index increment method, corresponded quite well, as expected, with the composition of the monomer feed.

Hydrolysis

Attempts to hydrolyze copolymers in which the methyl methacrylate blocks were atactic were unsuccessful insofar as complete hydrolysis was not achievable. The limiting extent of hydrolysis was in the region of 85%.

It was then hoped that the observation of Smets and Loecke,⁵ namely, that isotactic poly(methyl methacrylate) was hydrolyzable completely, would be useful. These authors used concentrated sulfuric acid as the hydrolyzing medium. When this procedure was applied to the styrene/methyl methacrylate copolymers, charring occurred (presumably the result

of attack by the strong acid on the polystyrene segments). Glavis¹⁰ has also studied the hydrolysis of isotactic poly(methyl methacrylate), in both acid and alkaline media. The (heterogeneous) alkaline hydrolysis did not proceed to completion. Under acid conditions, however, a modification of the method of Katchalsky and Eisenberg⁴ proved successful.

Although the methyl methacrylate homopolymers are soluble in this mixture, the copolymers prepared in the present work are not, due to the incompatibility of the water and the styrene segments of the copolymer.

TABLE I
Block Copolymers of Styrene with Methyl Methacrylate and Methacrylic Acid

Methyl methacrylate copolymer, mole-% styrene			Methacrylic acid copolymer, mole-% styrene
Monomer feed ^a	UV method	dn/dc method	Titration method
5	5.9	—	5.5
12.5	12.6	14.0	13.9
20	21.2	21.8	20.7
25	31.3	30.4	30.0
32.5	34.8	38.6	29.7
40	42.0	41.0	41.6
42.5	49.1	46.5	49.1
45.0	51.6	49.0	51.3
47.5	54.2	54.0	—
50	52.7	53.5	52.0
55	62.0	58.6	54.0
60	63.0	64.0	64.0
67.5	63.7	61.0	—
70	75.0	76.5	77.0
75	80.0	80.5	—
87.5	87.4	—	—

^a The figures in this column are approximate. Because of the limited accuracy of the monomer measurements by syringe, they are useful as a guide only.

Accordingly, water was omitted from the starting mixture and was instead added dropwise to the refluxing mixture in quantity such that the polymer was not precipitated. In later experiments, the water was omitted entirely without detriment to the results, indicating that it is not an essential ingredient.

In the cases of those polymers whose styrene content was above 80%, dimethylformamide was added to the refluxing system until complete solution was achieved. Absence of ester peaks at 1727 cm^{-1} in the neutralized products showed that hydrolysis was complete. This is confirmed by the direct determination of methacrylic acid units in the hydrolyzed polymers. The good agreement (see Table I) with the amount of methyl methacrylate in the unhydrolyzed polymer also indicates that hydrolysis is essentially complete.

The procedure outlined thus provides a convenient method for the preparation of block copolymers of styrene and methacrylic acid, at least in the low molecular weight region. Molecular weight measurements were not carried out on the samples prepared, but the conditions of preparation suggest that values in the region of 1200 would be obtained.

Tacticity measurements were not attempted on the copolymers. However, NMR studies on the poly(methyl methacrylate) homopolymer prepared under similar conditions, viz., same solvent, same temperature, fluorenyllithium as "initiator," indicated about 65% isotacticity. Observation of IR spectrum and glass transition temperature, although not giving a numerical estimate of tacticity, also suggested a high degree of isotacticity. It may be, therefore, that complete isotacticity is not an essential condition for complete hydrolysis.

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