Preparation of Block Copolymers
of Styrene and Methacrylic Acid

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Synopsis

A range of block copolymers of styrene and methacrylic acid has been prepared by the
suspension method involving migration of a growing radical across a phase boundary.
The way in which copolymer composition varies with change in the amount of the two
monomers in the reaction mixture has been studied, and explanations are suggested to
account for these variations. Two methods, involving calculation from solubility data
and thermogravimetric analysis respectively, have been used to give an estimate of the
length and composition of the blocks.

The preparation of block copolymers can be achieved by a method
involving the migration of a growing polymer radical across a phase bound-
ary. The method is applicable in those cases where the two monomers
show markedly different solubilities in an appropriate solvent which will
contain one monomer in solution with the other finely dispersed in this
solution with the aid of a dispersing agent. Initiation occurs in the con-
tinuous phase, followed by a period of radical growth. Some of these
growing radicals may terminate in the continuous phase, but others will
migrate across the phase boundary into the suspended droplets where
further polymerization and, eventually, termination occurs. The method
was first reported by Dunn and Melville,[1] who used it to make copolymers
of styrene with acrylic and methacrylic acids. The method was subse-
quently used by Hart and de Pauw[2] who prepared copolymers of vinyl
acetate and methacrylic acid. Although occasional later reports have
appeared,[3-5] the method has received relatively little attention. The
present paper is concerned with the application of the method to styrene
and methacrylic acid and in particular with the effect on the composition of
the copolymer of varying the initiator concentration and the composition of
the reaction mixture.

EXPERIMENTAL

Preparation and Purification of Materials

Styrene. Commercial styrene was purified by washing first with $2M$
sodium hydroxide solution to remove the inhibitor and then with distilled

water until the washings were neutral to litmus; it was then dried over anhydrous sodium sulfate for 3–4 hr. The dried styrene was vacuum-distilled in a nitrogen atmosphere, the middle fraction of the distillate being retained and stored in a refrigerator.

Methacrylic Acid. Methacrylic acid, obtained from Koch-Light Laboratories Ltd., was vacuum-distilled in a nitrogen atmosphere, the middle fraction of the distillate being collected and stored in a refrigerator.

Sodium Lauryl Sulfate. Anhydrous sodium lauryl sulfate was obtained from the Sigma Chemical Company and was used without further treatment.

Potassium Persulfate. Potassium persulfate was obtained from the May and Baker Chemical Company and was used without further treatment.

Benzoic Acid. Analar benzoic acid was obtained from B.D.H. Ltd., and was purified by recrystallization from ether and dried and stored in a desiccator over silica gel.

Ethanol. Absolute ethanol was used without further treatment.

Benzene. Benzene was dried over sodium for several days and then distilled from the sodium in a nitrogen atmosphere. It was stored under dry nitrogen in a tightly stoppered container to prevent access of carbon dioxide or water vapor.

Sodium Ethoxide Solution. A 5-g portion of clean dry sodium was dissolved in 100 ml absolute ethanol, precautions being taken to prevent ingress of carbon dioxide and water vapor. The mixture was kept cool and, after dissolution of the sodium, filtered and diluted with a further 150 ml absolute ethanol and 1000 ml sodium dried benzene. The solution was stored in a tightly stoppered bottle under dry nitrogen.

Preparation of Copolymers

Methacrylic acid was dissolved in 100 ml deionized water at 60°C and to this solution initiator, potassium persulfate, and stabilizer, 0.2 g sodium lauryl sulfate, were added. The stabilizer was used at a concentration below its critical micelle concentration. Styrene was dispersed in this solution by stirring and the temperature was held at 60°C for 2 hr. An atmosphere of nitrogen was maintained throughout. The product was a milky white suspension.

The polymer was coagulated from this mixture, by adding methanol, as a granular solid although in those cases where the mole percentage of methacrylic acid in the polymer was greater than 45% the precipitate was very finely divided and had to be coagulated before filtration. 0.1M hydrochloric acid was used as the coagulant. The solid product was thoroughly washed with methanol and then with water to remove the hydrochloric acid. The polymers were dried *in vacuo* at 40°C.

Three series of experiments were carried out, in all of which the volume of water and amount of stabilizer were kept constant. In each series one of

the three variables, initiator concentration, methacrylic acid concentration, or amount of styrene, was varied while the other two were kept constant.

Analysis

The total methacrylic acid content of the copolymers was determined by the method below, based upon that of Chang and Morawetz.[6] The solvent mixture (90 parts benzene/10 parts ethanol, by volume) used by these workers was not satisfactory in our case, and an 80/20 mixture was used instead. This was presumably due to the much wider range of methacrylic acid contents of our copolymers. This solvent mixture sufficed for all copolymers except those containing more than 90 mole-% methacrylic acid, for which absolute ethanol was employed.

An accurately weighed amount (ca. 0.1 g) of the copolymers was dissolved in 25 ml of the solvent, and the resulting solution was titrated with sodium ethoxide solution under dry nitrogen, thymol blue being used as indicator. Prior to each use the sodium ethoxide solution was standardized against purified benzoic acid.

The partition coefficient of methacrylic acid between water and styrene at 60°C was determined by equilibrating aqueous methacrylic acid and styrene under conditions similar to those used in the polymerizations but in the presence of an inhibitor and without initiator. Samples of each phase were removed and the concentration of methacrylic acid determined by titration with standard sodium hydroxide solution. The partition coefficient was also measured with poly(methacrylic acid) present in the aqueous phase.

The thermogravimetric work was carried out by use of a Stanton Nichrome furnace and recorder, the sample temperature being determined by using a chrome–alumel thermocouple and a potentiometer. A sample of the polymer (0.1–0.3 g) was accurately weighed into a porcelain crucible which was then placed in the furnace which had previously been heated to 230°C. Degradation was allowed to proceed at this temperature until no further weight loss, automatically recorded by the instrument, occurred. The percentage weight loss was calculated in each case.

The solubility of styrene in aqueous solution of methacrylic acid was determined by equilibrating styrene and methacrylic acid solutions at 60°C, separating the layers, and polymerizing the aqueous layer to completion. The copolymer was isolated by evaporation and analysed by titration as already described. From this result the amount of styrene originally present was calculated.

RESULTS AND DISCUSSION

The results of the preparations in which the initiator concentration was varied are shown in Figure 1, from which it is evident that the copolymer composition is essentially independent of initiator concentration. The copolymer composition is thus a function of the two monomer concentrations.
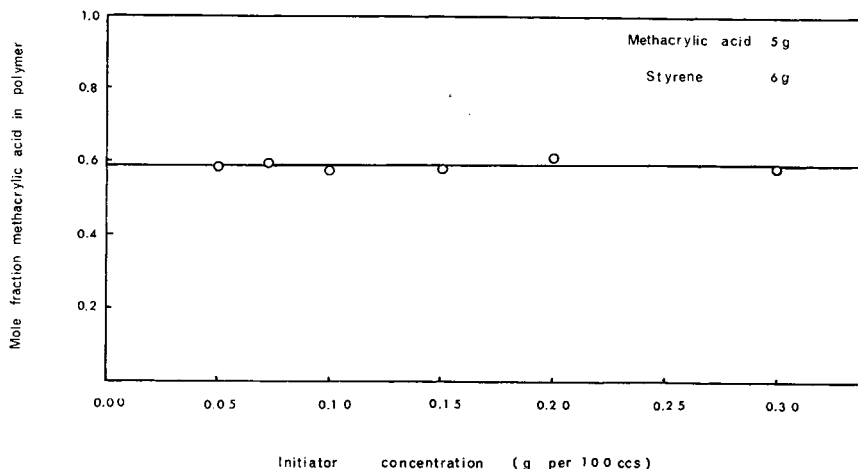
Fig. 1. Copolymer composition vs. initiator concentration.

The results of the preparations in which the styrene/aqueous phase ratio was kept constant while the methacrylic acid concentration was varied are illustrated in Figure 2. Curve I shows the composition of the copolymer, expressed as mole fraction methacrylic acid present, as a function of the amount of methacrylic acid in the reaction mixture.

The copolymer compositions plotted on curve I, obtained by sodium ethoxide titration, represent the total amount of methacrylic acid present in the copolymer and do not yield information about the relative lengths and compositions of the blocks. The latter will depend upon the mutual solubility of the two phases. Because of this mutual solubility each block consists of a random copolymer of the two monomers. In what follows,
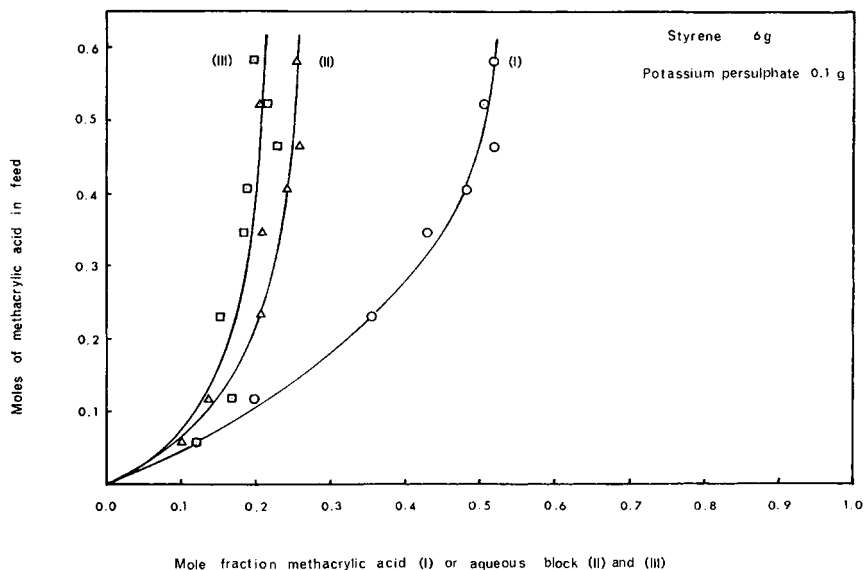
Fig. 2. Copolymer composition vs. number of moles methacrylic acid in reaction mixture.

that part of the copolymer formed in the aqueous phase will be referred to as the aqueous block, and that part formed in the styrene phase will be called the styrene or nonaqueous block.

Some indication of the effect of the mutual solubilities on block composition may be obtained from the copolymer composition equation,[7] coupled with a knowledge of the mutual solubilities. The partition of methacrylic acid between water and styrene at 60°C follows the usual law, indicating that the acid is dimerized in the styrene phase. It was found that

$$[\text{methacrylic acid}]_{aq}/[\text{methacrylic acid}]_{1/2\ \text{styrene}} = 0.363$$

The value of the constant is unaffected by the presence of poly(methacrylic acid) dissolved in the aqueous layer. The solubility of styrene in various concentrations of aqueous methacrylic acid is shown in Figure 3. The value for pure water has been extrapolated from those measured by Bovey and Kolthoff.[8] By using the solubilities thus obtained, the initial compositions of the aqueous and styrene blocks can be obtained from the copolymer composition equation from known values for the reactivity ratios.[9] As expected from the low solubility of styrene in the aqueous phase, the amount of styrene in the aqueous block is quite small, usually
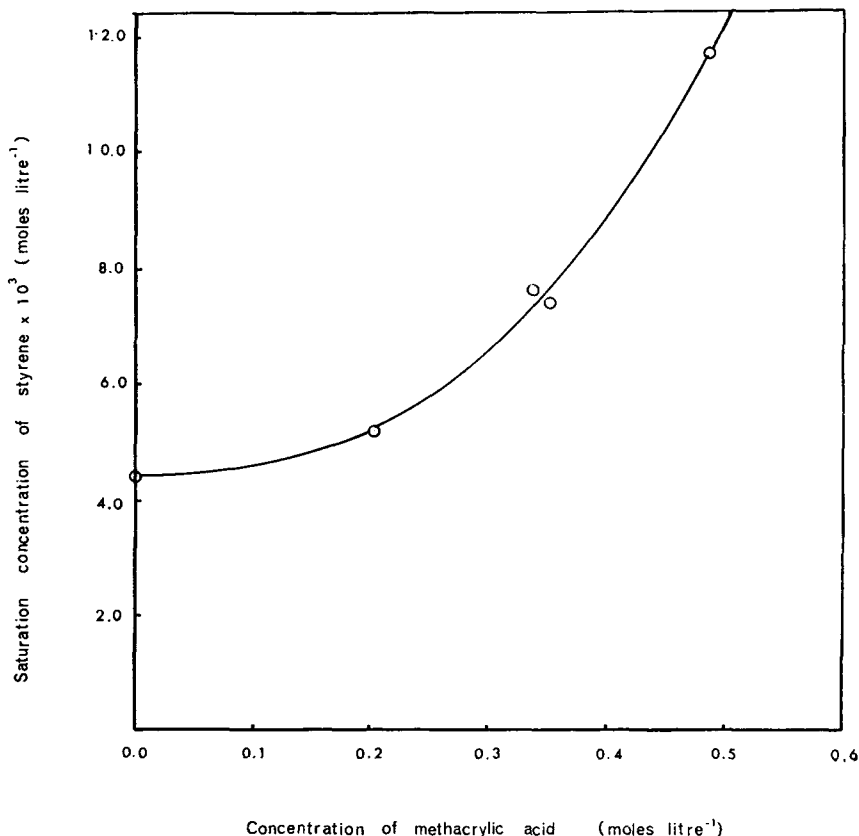

Fig. 3. Saturated solubility of styrene vs. concentration of methacrylic acid.

about 3 mole-%. These block compositions coupled with the overall compositions as determined by titration enable the relative block lengths to be calculated. The results of these calculations are shown by curve II of Figure 2, where the mole fraction of the aqueous block is plotted against the amount of methacrylic acid in the reaction mixture.

The use of such calculations as a guide to the final copolymer composition must, however, be regarded with some reserve since the solubility values on which the calculations were based are those pertaining to the initial conditions. As polymerization proceeds, the values of the relative monomer concentration may drift due to the changing conditions and this, in turn, may affect the copolymer composition.

In view of the uncertainty attached to these calculations, an alternative method of determining the block lengths was sought. It has proved possible to do this by a thermogravimetric procedure based on the work of Grant and Grassie,[10] who showed that at 200°C poly(methacrylic acid) is converted into the anhydride. They also showed that anhydride formation occurred almost exclusively between adjacent methacrylic acid units with negligible formation of crosslinks or large rings.

It was found, in agreement with the results of Grant and Grassie, that the loss in weight during anhydride formation was considerably greater than the theoretical value (due to absorbed moisture) and the results below were obtained by using the loss from poly(methacrylic acid) itself as a reference value. The most satisfactory results were obtained at a slightly higher temperature (230°C).

In a styrene–methacrylic acid copolymer the formation of anhydride would occur only between adjacent pairs of methacrylic acid units. In a homogeneous block of methacrylic acid units complete conversion to anhydride would be possible and the weight loss would be directly related to the relative lengths of the styrene and methacrylic acid blocks. Table I shows the results obtained with some copolymers containing homogeneous blocks (prepared by Dunn and Melville,[1] chain transfer method).

In a random copolymeric block, on the other hand, conversion to anhydride would be incomplete because of separation of some of the methacrylic units by styrene units. The calculation of the fraction of acid units capable of anhydride formation is analogous to that carried out by Wall[11] on copolymers of vinyl chloride and vinyl acetate with a view to obtaining the fraction of chlorine atoms removable by reaction with zinc (only chlorine atoms in adjacent units being capable of reaction). Such calcula-

TABLE I
Determination of Length of Horropolymeric Blocks of Methacrylic Acid

Copolymer composition, mole-% methacrylic acid	
By titration	By thermogravimetric analysis
0	0
40.8	40.5
56.8	52.0
86.8	87.5

tions show that in random copolymeric blocks containing less than about 15 mole-% methacrylic acid the actual loss in weight would be extremely small, and the observed loss in weight of the copolymer can be used as a measure of the length of the aqueous block.

The use of this procedure may involve some error in those cases where the styrene block contains more than 15 mole-% methacrylic acid. The importance of this error will be diminished by the tendency towards alternation in the random copolymeric blocks. Wall's calculation is strictly applicable to copolymers which are ideal, i.e., have a completely random distribution of units, the criterion for which is that the product of the reactivity ratios should equal unity. In the present case this product (0.105) is appreciably less than unity, indicating a tendency for the units to alternate, in which case the fraction of acid groups convertible to anhydride will be even less than the calculations suggest, especially in those copolymers containing smaller amounts of methacrylic acid.

The lengths of the aqueous blocks estimated in this way are also shown on Figure 2 (curve III). It can be seen that the values determined this way are in broad agreement with those calculated from the solubility measurements by means of the composition equation.

The graph shows that the length of the aqueous block tends to a constant value as the amount of methacrylic acid in the feed is increased. This result can be explained in the following manner. The length of an aqueous radical will depend upon the concentration of methacrylic acid in the aqueous phase, other parameters remaining constant, and increasing the methacrylic acid concentration will tend to increase the length of the aqueous block because of the greater length of these radicals just prior to diffusion into the styrene phase. However, larger radicals will diffuse into the styrene phase more slowly than smaller ones and this effect will be more pronounced the greater the average length of the radicals. There will thus be a "fractionation effect" which becomes more pronounced at higher methacrylic acid concentrations. Diffusion effects are a well known feature of acrylic polymerizations.[12]

Results for the other series of preparations in which the styrene feed was varied are depicted in Figure 4, the three curves having the same significance as in Figure 2, i.e., I denotes mole fraction of total methacrylic acid, II denotes mole fraction of aqueous block as calculated from mutual solubilities, and III denotes mole fraction of aqueous block as determined thermogravimetrically.

It can be seen from Figure 4 that when the amount of styrene in the feed is low, relatively small increases in the amount of styrene produce quite large increases in the size of the styrene block. Several factors are likely to contribute to this result, viz. (1) with the suspended styrene droplets increased in number and/or size, the growing radicals in the aqueous phase will tend to be shorter as a result of increased opportunity to enter the styrene phase; (2) the concentration of growing radicals in the styrene phase will decrease as the volume of this phase increases and the rate of termination will decrease. giving larger radicals; (3) with a greater volume
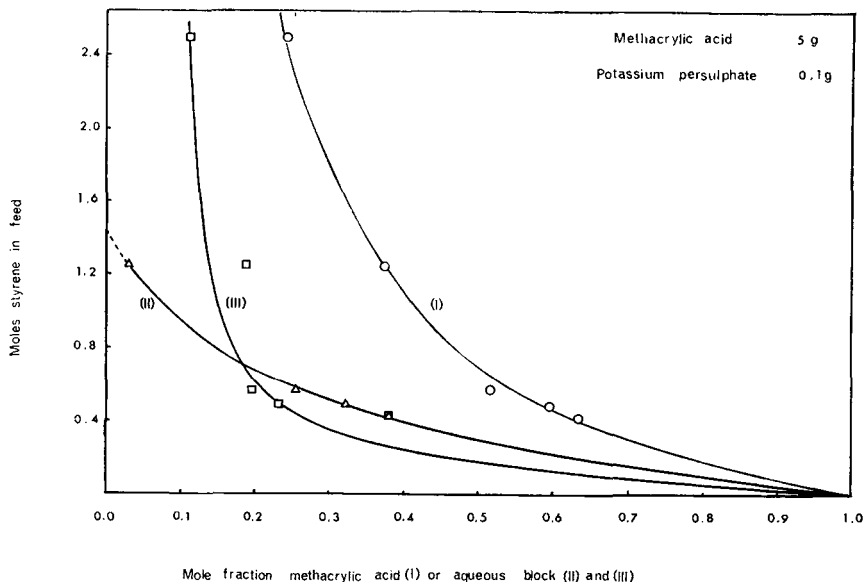
Fig. 4. Copolymer composition vs. number of moles styrene in reaction mixture.

of styrene, the concentration of methacrylic acid in the aqueous phase will be lower as a result of partition.

It can be seen from Figures 2 and 4 that, except where the volume of styrene is very high, when the compositions calculated from solubility data are clearly unrealistic (curve II on Figure 4, a negative fraction of aqueous block being obtained in one case), the compositions estimated by the solubility method are quite close to those found by thermogravimetric analysis. This encourages the belief that although both methods are subject to some uncertainty, they do, nevertheless, provide a reasonable guide to block length and composition in the copolymers.

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