

Styrene + Methyl Methacrylate Block Copolymers

Part 1.—Preparation and Fractionation

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Styrene has been polymerized in bulk at 60°C using *m*-di-isopropyl benzene dihydroperoxide as initiator to give a polymer with single hydroperoxy end-groups. The polymer has been fractionated by precipitation from methyl ethyl ketone with methanol to give samples with narrow molecular weight distributions in the region of 1.6×10^5 determined osmotically and viscometrically.

This polystyrene has been used to initiate the polymerization of methyl methacrylate in emulsions at 8°C in the presence of ferrous sulphate. A block copolymer was formed in this way and separated from unchanged polystyrene by fractional precipitation from benzene with methanol. The block copolymer was split into a number of fractions with narrow distributions of molecular weight and chemical composition using solvent gradient elution from a column packed with glass beads. The chemical compositions of these fractions were determined by ultra-violet spectrophotometry, chemical analysis for carbon and oxygen, and from comparison of the molecular weights of the styrene polymer and block copolymer.

Evidence is discussed for presuming that the fractions obtained consisted mainly of simple block copolymers containing a single sequence of each type of monomer in every molecule.

During the past decade many methods for the synthesis of block copolymers have been published; among various reviews are those of Hart, Smets, Gaylord and Burnett.¹ Little has appeared, however, concerning studies of the solution properties of these copolymers. A thermodynamic study of such solutions requires well-defined fractions of copolymer of precisely known monomeric composition and molecular weight. Such fractions are not easily obtained from any of the early syntheses as the yields are low and little control can be exercised over the composition of the block copolymers produced.

An apparently attractive route to block copolymers is to link two different and well-characterized homopolymers through reactive end-groups. Solution properties are best studied using high molecular weight fractions and for these the concentration of end-groups is too low for good yields. An alternative is to make one polymer with end-groups still capable of behaving as initiators and to fractionate this with respect to molecular weight. A second monomer may then be added to a particular fraction and polymerization restarted. Although the product has to be refractionated, the fractions so obtained are then uniform with respect to both molecular weight and monomeric composition.

There are several methods available giving a stable product for the first stage which can be fractionated by standard methods before proceeding to the second stage.² In this paper the preparation of styrene+methyl methacrylate block copolymers using the dihydroperoxide method³ is described. The products have been fractionated by an elution column method. The viscosities in toluene and methyl ethyl ketone and the osmotic pressure in toluene as a function of temperature and concentration have been examined for several of the fractions. These are considered in the following paper.

EXPERIMENTAL

MATERIALS

STYRENE AND METHYL METHACRYLATE

The inhibitors were removed from the monomers by washing with caustic soda solution in the ratio 4:1. The monomers were then washed with distilled water and dried over anhydrous sodium sulphate. The dried monomers were distilled under oxygen-free nitrogen at reduced pressure. For styrene, the fraction boiling at 45°C under 20 mm Hg pressure was collected; for methyl methacrylate the fraction had a boiling point of 35°C at 66 mm Hg pressure. These monomers were stored under nitrogen at -10°C.

m-DI-ISOPROPYL BENZENE DIHYDROPEROXIDE

The dihydroperoxide was provided by Dr. A. M. North. It was crystallized from ethanol and stored at -10°C. The purity was greater than 94 % as determined by an iodometric technique.⁴

MANOXOL OT

This emulsifier presented by Hardman and Holden Ltd. was in the form of 60 % aqueous gel of dioctyl sodium sulposuccinate.

SOLVENTS

The solvents used were A.R. benzene, chloroform, toluene and methyl ethyl ketone. They were dried and distilled before use.

POLYMERIZATION OF STYRENE

Thermal decomposition of the initiator was used to prepare polystyrenes with hydroperoxy end-groups. The temperature was kept as low as possible to minimize the amount of purely thermal (and hence inactive) polystyrene produced, and the decomposition of the second hydroperoxide group of the initiator. The steric effect of the growing polymer chain may help to prevent the simultaneous decomposition of the two hydroperoxide groups. Once polymer molecules with hydroperoxy end-groups have been formed, however, there is a possibility of some thermal decomposition of the second hydroperoxide group taking place leading to polystyrene incapable of initiating polymerization of methyl methacrylate in the second stage of the synthesis.

All polymerizations were carried out under vacuum. Styrene monomer was outgassed by alternate freezing, pumping and melting three times, and was then distilled into a flask where it was prepolymerized for 30 min using a 125-W Osira lamp to remove any peroxides still present. The monomer was then distilled into a graduated flask.

The reaction vessel was a 100-ml round-bottomed flask fitted with a side-arm through which a weighed amount of the dihydroperoxide initiator was introduced. The side-arm was sealed and the vessel and its contents outgassed before 50 ml styrene were distilled from the graduated flask. The vessel was sealed under vacuum and transferred to a thermostat regulated to $60 \pm 0.02^\circ\text{C}$. The monomer was allowed to polymerize with occasional shaking for 2 to 3 h.

The contents of the reaction vessel were then diluted with 50-60 ml benzene and slowly added, with continuous stirring, to 400 ml methanol. Care was necessary to ensure that the precipitated polymer was uncontaminated by unreacted initiator which would give rise to homopolymer in the second polymerization stage. The polymer was therefore redissolved in benzene, reprecipitated with methanol and washed repeatedly with more methanol before being dried under vacuum. Table 1 gives details of some of the preparations of polystyrene.

Attempts to determine the hydroperoxide content of the polystyrene by means of the colorimetric method of Takayama⁵ or by an iodometric method⁴ were not successful as the concentration of the hydroperoxide groups (1 or 2 per polymer chain) was too low to give accurate determinations.

TABLE 1.—POLYMERIZATION OF STYRENE AT 60° WITH *m*-DI-ISOPROPYL BENZENE DIHYDRO-PEROXIDE INITIATOR

expt. no.	vol. styrene (ml)	initiator concn. (mmole/l.)	reaction time (min)	polymer yield (g)
S10	50	3.52	155	2.61
S13	48	3.46	160	2.24
S15	50	3.56	165	2.69
S17	50	3.55	170	3.01

FRACTIONATION OF POLYSTYRENE WITH HYDROPEROXY END-GROUPS

An approximately 1.5 % solution of the polystyrene in methyl ethyl ketone was prepared and methanol slowly added with continuous stirring at room temperature until a turbid solution was obtained. This was gently warmed till the turbidity disappeared and then allowed to cool slowly. The precipitate was separated by centrifuging at 550 g and retained as the first fraction. The supernatant liquid was treated with further methanol to give a second fraction. This procedure was followed until all the polymer had been recovered.

The precipitation range of any fraction is given by the upper and lower volume fractions of precipitant γ where

$$\gamma = \frac{\text{volume of precipitant}}{\text{volume of precipitant} + \text{volume of solvent}}.$$

Table 2 shows the results obtained for the fractionation of two typical polystyrenes. For each polymer the largest fraction was obtained for the γ range 0.15-0.18.

Viscosity measurements were used to give an indication of the efficiency of the fractionations. The viscosities of the fractions in toluene were measured at 25° using an Ostwald viscometer. Fig. 1 shows η_{sp}/c against c curves obtained for the fractions of S16. The

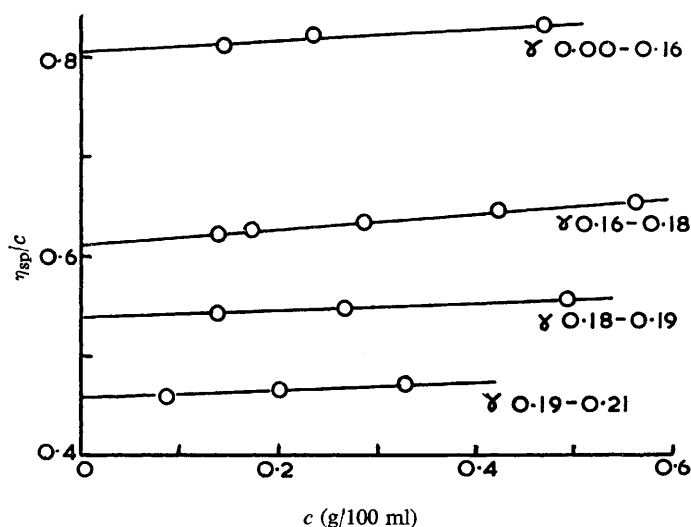


FIG. 1.— η_{sp}/c against concentration c for fractions of polystyrene S16 precipitated between the volume fractions γ of methanol indicated.

intrinsic viscosities and hence the molecular weights of the fractions decreased as γ increased showing that a separation had been achieved. Since the polystyrenes were prepared under almost identical conditions, their molecular weight distributions should have been similar. This is confirmed by fig. 2, which shows η_{sp}/c against c plots for similar fractions from different polymerization batches, and by the precipitate weights in table 2.

MOLECULAR WEIGHT OF POLYSTYRENE FRACTIONS

Number average molecular weights \bar{M}_n were obtained from osmotic pressure measurements in toluene at 25°C. Viscosity average molecular weights \bar{M}_v were calculated from the intrinsic viscosities $[\eta]$ using the equation of Oth and Desreux ⁶

$$[\eta]\bar{M}_v^{-\frac{1}{2}} = K^{\frac{1}{2}} + C_T K^{\frac{1}{2}} \bar{M}_v [\eta]^{-1}. \quad (1)$$

The quantities K and C_T for polystyrene in toluene at 25° have been determined from the data of Outer, Carr and Zimm;⁷ they are $K = 8.0 \times 10^{-4} \text{ mole}^{\frac{1}{2}} (100 \text{ ml})^{\frac{3}{2}} \text{ g}^{-2}$, $C_T = 27.79 \times 10^{-4} \text{ mole}^{\frac{1}{2}} (100 \text{ ml})^{-\frac{1}{2}} \text{ g}$.

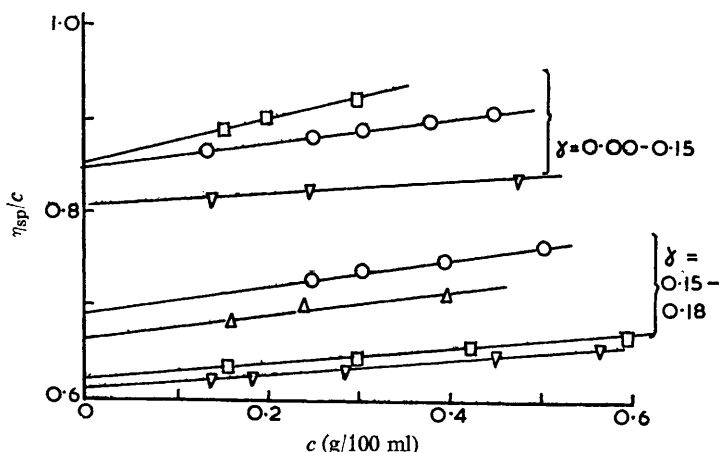


FIG. 2.— η_{sp}/c against concentration c for fractions of the several polystyrene samples indicated precipitated under similar conditions.

□=S17; ○=S10; ▽=S16; △=S13.

\bar{M}_n and \bar{M}_v are compared in table 3 for a variety of fractions from several batches of polystyrene. \bar{M}_v/\bar{M}_n always lay between 1.03 and 1.10 indicating that a satisfactorily sharp fractionation had been achieved.

TABLE 2.—FRACTIONAL PRECIPITATION OF POLYSTYRENE FROM METHYL ETHYL KETONE WITH METHANOL (γ = VOLUME FRACTION METHANOL)

γ range	% polystyrene precipitated					
	sample S13		sample S16		sample S17	
0.00-0.15	5.5	7.8	7.3	6.0	4.8	7.3
0.15-0.18	59.6	57.7	31.0	43.4	33.0	28.3
0.18-0.19	25.8	24.0	26.0	17.3	27.5	20.8
0.19-0.21	5.8	2.6	11.8	10.1	22.2	13.9
0.21-0.23	2.1	2.0	10.8	8.7	6.5	12.1
0.23-0.26	—	—	5.3	5.3	1.3	7.1
% recovered	98.8	94.1	92.2	90.8	95.3	89.5

PREPARATION OF STYRENE+METHYL METHACRYLATE BLOCK COPOLYMER

Thermal decomposition of the hydroperoxy-ended polystyrenes in the presence of a second monomer would lead to a large amount of homopolymer in addition to block copolymer due to the production of two radicals $RO\cdot$ and $HO\cdot$, each capable of initiating polymerization. This difficulty was overcome by using a redox initiating system. Fordham

and Williams⁸ and Orr and Williams⁹ have studied the kinetics of the decomposition of cumene hydroperoxide by ferrous ion in dilute solution in the presence of acrylonitrile. Under these conditions the hydroperoxide and ferrous ion disappear only by means of the reaction,



Capture of the $\text{RO}\cdot$ radical by monomer suppresses the radical induced oxidation of Fe^{2+} and the induced decomposition of hydroperoxide. Since the hydroperoxy-ended polystyrene has an end-group similar to that of cumene hydroperoxide, ferrous-ion-induced decomposition of the polymeric material should take place giving polymeric hydroperoxy radicals capable of initiating polymerization.

TABLE 3.—COMPARISON OF VISCOSITY AVERAGE \overline{M}_v AND NUMBER AVERAGE \overline{M}_n MOLECULAR WEIGHTS OF POLYSTYRENE FRACTIONS

sample	γ range	$\overline{M}_v \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_v/\overline{M}_n$
S10	0.15-0.18	1.84	1.75	1.05
S13	0.15-0.18	1.76	1.68	1.05
S15	0.15-0.18	1.61	1.50	1.07
S17	0.15-0.18	1.57	1.50	1.05
S13	0.18-0.19	1.47	1.34	1.10
S15	0.18-0.19	1.30	1.26	1.03
S17	0.18-0.19	1.26	1.20	1.05

The reaction vessel used for these polymerizations consisted of a 250-ml round-bottomed flask A and a 150-ml round-bottomed flask B, each fitted with a side-arm and joined to a horizontal tube connecting with a vacuum system so that flask A was above flask B. A weighed amount of hydroperoxy-ended polystyrene was introduced into flask A and the side-arm sealed off. Into flask B was introduced an aqueous solution of the emulsifying agent Manoxol OT and an aqueous solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, acidified with dilute H_2SO_4 . The contents of flask B were outgassed, the side-arm sealed off and the solution frozen in liquid nitrogen. Flask A was then surrounded by a liquid nitrogen bath and methyl methacrylate distilled into it. Since flask A was nearer the methacrylate source than B, the monomer collected in A.

The reaction vessel was sealed off under vacuum and by carefully melting the contents of the two flasks it was possible to prevent water distilling into the monomer, or vice versa. In this way monomer and aqueous solution were kept separate till the polymer had dissolved in the monomer. The contents of the flasks were then thoroughly shaken together and the reaction vessel placed in a thermostat at 8°C for 5-6 h. To isolate the product the reaction mixture was poured into benzene and the liquid was then added slowly, with stirring, to a large volume of methanol. The precipitate was collected by filtration, washed with methanol to ensure removal of emulsifier, and dried on a low vacuum line. Some preliminary experiments using unfractionated polystyrene indicated the reaction conditions for which the average composition of block copolymer was just over 50 % polystyrene.

The polystyrene fractions used in this second stage of the block copolymer synthesis were those collected over the γ -range 0.15-0.18. Experiment 13SFM therefore used the fraction obtained from polystyrene S13 over this γ range, and so on. The copolymerization results shown in table 4 are fairly consistent with the increase in weight on copolymerization ranging from 46 % to 69 %. Assuming no inactive polystyrene to be present, the average composition of the block copolymer was 66 % polystyrene.

FRACTIONATION OF BLOCK COPOLYMER

Before any block copolymer can be identified and characterized it is necessary to separate it from homopolymers. This can best be achieved by means of fractional precipitation from solution. Dunn, Stead and Melville¹⁰ showed, by means of a turbidimetric titration,

that styrene+methyl methacrylate block copolymer may be separated from the homopolymers in acetone solution using distilled water as precipitant. This solvent+precipitant system isolates the three fractions over such a narrow range of precipitant concentration that it is difficult to achieve a complete separation.

A study of the benzene+methanol system was considered more useful. Experiments showed that when methanol was added to a 1 % solution of unfractionated polystyrene and polymethyl methacrylate homopolymers, containing 35 % by weight of styrene, addition of 40 % by volume methanol precipitated all the polystyrene but no methyl methacrylate was precipitated until at least 70 % by volume of methanol had been added. In most cases, therefore, the precipitation of polymer in the range from 40-70 % methanol would indicate the presence of block copolymer.

Fractional precipitation using benzene+methanol was carried out on the products of table 4. In every case, block copolymer was shown to be present. Details of two parallel experiments are given in table 5; the compositions were determined by ultra-violet

TABLE 4.—PREPARATION OF BLOCK COPOLYMERS

expt.	polystyrene (g)	methyl metha- crylate (g)	total reaction mixture			time (min)	reaction product	
			Fe ⁺ (mmole/l.)	Manoxol (g)	water (ml)		yield (g)	weight increase, %
13SFM	0.81	26.3	7.84	0.43	50	330	1.20	48
14SFM	0.82	26.3	7.84	0.42	50	330	1.32	61
15SFM	0.78	28.2	6.80	1.10	60	360	1.25	60
16SFM	0.84	28.2	7.40	1.10	60	340	1.42	69
17SFM	0.70	37.6	5.47	0.85	60	345	1.02	46
18SFM	0.82	37.6	5.94	0.83	60	330	1.30	58

absorptiometry. The compositions of these copolymers were promising for the study of block copolymer properties. For example, approximately 50 % of the polymer in 14SFM had a composition ranging from 40 to 75 % polystyrene. The bulk products were therefore given a preliminary separation from homopolymers by means of fractional precipitation using this system. Methanol was added to a 1 % solution of the polymer in benzene until there was 35 % precipitant. The precipitate was removed by centrifuging and contained mainly the styrene homopolymer. More methanol was added to the remaining solution until the percentage precipitant was 75 %. The main content of this precipitate was the block copolymer.

TABLE 5.—PRELIMINARY FRACTIONAL PRECIPITATION OF BLOCK COPOLYMER 14SFM FROM BENZENE WITH METHANOL (γ = VOLUME FRACTION OF METHANOL)

γ range	experiment A		experiment B	
	% polymer pptd.	styrene content, %	% polymer pptd.	styrene content, %
0.00-0.35	35.0	86.2	37.8	88.0
0.35-0.42	27.1	71.5	25.2	76.6
0.42-0.50	7.2	58.1	9.4	59.3
0.50-0.58	12.6	49.9	11.2	51.2
0.58-0.64	4.9	36.7	5.3	39.4
0.64-0.70	2.6	19.3	3.8	18.1
0.70-0.76	6.1	7.0	5.3	5.9
% recovered	95.5		98.0	

This copolymer was sharply fractionated using the so-called chromatographic fractionation of high polymers.¹¹ The apparatus used here was a modification of that described by Hartley.¹² A solvent reservoir A (2 l. capacity) was connected to a mixing vessel B (1.2 l. capacity) by means of a constant level syphon, as shown in fig. 3. The mixing vessel was connected through a diaphragm tap to the top of the fractionating column D. The chamber B was filled with sufficient non-solvent to just cover a small hole near the end of the syphon tube C. As the non-solvent flowed down the column this hole was uncovered,

air travelled up the tube and solvent flowed from the reservoir A into B until the hole was covered again. The liquid in the mixing chamber was continuously circulated through a glass centrifugal pump. The advantage of this stirring arrangement was that the liquid level in the mixing vessel remained constant and undisturbed.

The column was a glass tube 2 cm in diam. and 36 cm long widened at the top into a tube 4 cm in diam. and 7 cm long. A no. 2 sintered-glass disc was fitted near the base of the column and the flow of liquid was controlled by means of a diaphragm tap below this disc. The narrower part of the column was packed with Ballotini no. 15 glass beads of average diameter 0.1 mm. A temperature gradient from 38° at the top to 22° at the bottom was maintained in this part of the column by a Nichrome heating tape wound round it. The wider part at the top of the column was kept at 36–37°C.

To ensure that the flow of liquid through the column was controlled only by the lower tap the system had to be airtight. This was achieved by heating the glass capillary tubes which fitted into the polythene diaphragm taps until a little of the polythene melted. On cooling the polythene-glass joints were firmly sealed. The mixing vessel was joined to the column through a B34 cone and socket-fitted with a Teflon sleeve and held together by spring clips.

The copolymer to be fractionated was deposited on to a spiral roll of stainless steel wire gauze. To do this, from 0.5 to 1.0 g of polymer was dissolved in 30–40 ml chloroform and placed in a shallow half-cylindrical basin. The gauze was wound into a spiral on a shaft which slowly rotated in the basin so that not more than half the spiral was immersed in the solution at any time. Solution adhered to the gauze as it emerged from the liquid and chloroform evaporated as that part of the gauze slowly rotated in the air. In this way, a film of polymer was deposited on the gauze, better than 92 % deposition being achieved.

The spiral was placed in the wider part of the column and a solid aluminium cylinder inserted down the middle of the spiral thus reducing the void volume of the gauze compartment from 88 to 22 ml. The gauze compartment and the column were flooded with non-solvent (usually 80 % methanol + 20 % benzene). Once the required temperature gradient had been established, the mixing chamber, solvent reservoir and stirrer were brought into position. The mixing chamber was filled with non-solvent of the same composition and the diaphragm tap at the foot of the column adjusted to give a flow rate of 6–7 ml/h. 25 ml fractions were removed by an automatic collector. The contents of the first two fractions were the initial non-solvent from the column which had a hold-up of 47 ml.

Each fraction was placed in a 100-ml tube with a ground-glass neck into which fitted a sintered-glass crucible with a side-arm below the disc. The side-arm was attached to a filter pump through a cold trap. The tube was supported in a water bath and the warm solution evaporated by drawing a stream of air over it until only 3–4 ml remained. Methanol was then added and the precipitated polymer collected by filtration and dried.

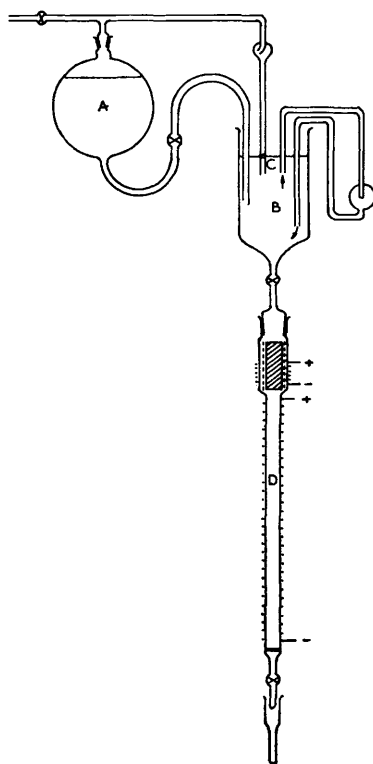


FIG. 3.—Block copolymer fractionating column.

FRACTIONATING COLUMN PERFORMANCE

Successful operation of the fractionating column required efficient stirring in the mixing vessel, a uniform composition throughout the gauze compartment and "plug flow" in

the bead-packed column. In view of the large volume of the mixing chamber (975 ml of liquid) and the slow flow rate down the column (7 ml/h), there is no doubt that the circulating pump agitated the liquid in the mixing chamber sufficiently. The slow flow rate also encouraged the correct flow conditions in the column. The main problem was to secure thorough mixing in the gauze compartment.

This could not be mechanically stirred without risk of detaching swollen polymer from the gauze. Thus, it was necessary to rely on convection currents to keep the liquid in motion. It was for this reason that a roll of gauze was chosen as a support for the polymer in preference to depositing it on glass beads, as had been done by several previous workers. The heater windings on the gauze compartment were concentrated near the bottom and the spiral roll of gauze placed with its axis vertical so as to impede as little as possible the convection currents. An attempt to confirm that the solvent composition gradient in the column had the desired form was made by withdrawing samples at intervals from the mixing vessel and fraction tubes and analyzing these by refractive index determination.

For the mixing vessel, the composition after V ml have flowed down the column and been replaced by solvent is given by

$$v_m = v^\circ \exp(-V/B_m), \quad (2)$$

where v_m is the volume fraction of non-solvent in the vessel, v° the volume fraction of non-solvent in the liquid with which the apparatus was filled initially and B_m is the constant volume of liquid in the vessel.

For the fraction collected from the base of the column over the range of volumes discharged from V_1 to V_2 , the volume fraction of non-solvent may be shown to be given by

$$v_f = \frac{v^\circ}{(B_m - B_g)(V_2 - V_1)} \left[B_m^2 \left\{ \exp\left(\frac{B_c - V_1}{B_m}\right) - \exp\left(\frac{B_c - V_2}{B_m}\right) \right\} - B_g^2 \left\{ \exp\left(\frac{B_c - V_1}{B_g}\right) - \exp\left(\frac{B_c - V_2}{B_g}\right) \right\} \right], \quad (3)$$

where B_g and B_c are the volumes of liquid always held in the gauze compartment and column respectively.

It was found that the observed values of v_m and v_f as functions of V followed (2) and (3) closely in form but there was a quantitative deviation (as though B_m were smaller than its true value) which was shown to be due to evaporation partly from the mixing vessel and partly at the fraction collector. Since $B_g \ll B_m$ the second term in the square bracket of (3) is very much smaller than the first and it was thus not possible to confirm from these analyses whether complete mixing was taking place in the gauze compartment.

FRACTIONATION RESULTS

The chromatographic fractionations were all performed on block polymers which had been separated from almost pure polystyrene by preliminary fractional precipitations. Table 6 gives the operational data for the chromatographic column. The histograms in fig. 4 show how the weight of polymer varied from fraction to fraction. The total recovery of polymer was 92.95 %.

TABLE 6.—ELUTION COLUMN DATA FOR BLOCK COPOLYMER FRACTIONATIONS

expt.	13SFM	15SFM	17SFM
weight of polymer fractionated (g)	0.69	0.66	0.46
% methanol in initial non-solvent	80.0	80.0	100.0
temp., °C:			
(a) gauze compartment	37	21	37
(b) column top	40	39	39
(c) column bottom	23	23	23
flow rate (ml/h)	6.5	6.0-6.5	6.5

ANALYSIS OF BLOCK COPOLYMER

Test experiments showed that the compositions of mixtures of styrene+methyl methacrylate homopolymers could be correctly estimated by spectrophotometric analysis using the absorption at 262 m μ by polystyrene. The specific extinction coefficient K of a polymer mixture is given by

$$K = xK_S + (1-x)K_M. \quad (4)$$

For the polystyrene+polymethyl methacrylate system

$$K = \frac{\text{optical density at 262 m}\mu}{\text{cell length (cm)} \times \text{conc. (g/l.)}}.$$

K_S is the specific extinction coefficient for polystyrene, K_M for polymethyl methacrylate and x is the fraction by weight of polystyrene. Optical density readings were obtained using a Unicam SP 500 spectrophotometer with chloroform as solvent.

This relationship is only true provided both components act independently with regard to the absorption of light. It was hoped that this condition would be obeyed for block copolymers, but it was possible that the effect of one chain could be modified by the presence of the other chemically bound to it. In an attempt to check upon this, two independent methods of determining the composition of the block copolymer fractions were used. They were chemical analysis and the determination of the osmotic molecular weights of the fractions. Both give results which do not depend on the arrangement of the monomer sequences in the copolymer.

Combustion analysis of the block copolymer gave the percentage carbon and hydrogen present. The percentage hydrogen could not be used to determine the styrene content, however, as it changes by only 0.3 % from 100 % polystyrene (H % = 7.7) to 100 % polymethyl methacrylate (H % = 8.0). For styrene, the percentage of carbon is 92.3 and for methyl methacrylate 60.0, hence C % in a styrene+methyl methacrylate copolymer could be used to determine the styrene content from

$$C \% = 32.3x + 60.0.$$

For a few fractions, a direct determination of the percentage of oxygen was kindly carried out by Dr. A. F. Colson of Imperial Chemical Industries Alkali Division. Since polystyrene contains no oxygen and polymethyl methacrylate contains 32 % hence

$$O \% = 32(1-x),$$

where O % is the percentage of oxygen in the copolymer.

The osmotic method depended upon the fact that fractionated polystyrene was used to prepare the block copolymer. Hence the ratio of the number average molecular weight of polystyrene to that of the resultant block copolymer gave the weight fraction of polystyrene present. The weights per cent of styrene (100x) in several block copolymer fractions obtained by these methods are compared in table 7 to illustrate the extent of agreement.

TABLE 7.—ANALYSES OF BLOCK COPOLYMER FRACTIONS

sample	fraction	% styrene by weight		second method *
		u.-v. analysis	second method	
13SFM	17	55.3	52.7	O
	24-26	72.5	75.5	\bar{M}_n
15SFM	18	52.5	45.5	C
	24	53.6	63.5	C
	25-27	52.8	47.4	\bar{M}_n
	28-30	53.5	57.8	\bar{M}_n
17SFM	26	58.6	57.3	C
	27	57.0	58.5	C
	28-30	63.0	65.4	\bar{M}_n
	30	61.5	62.2	C

* O, oxygen analysis; C, carbon analysis; \bar{M}_n , from molecular weight.

On the whole, the styrene contents of the block copolymer fractions determined by u.-v. absorption agreed with those obtained by chemical analysis and from the molecular weight method. Combustion analysis is always difficult with polymers and the molecular weight method, depending upon the ratio of the intercepts of two extrapolated osmotic pressure graphs, was subject to considerable experimental error. The u.-v. absorption measurements on the other hand were rapid and sensitive and so were used as the routine method for the analysis of all fractions.

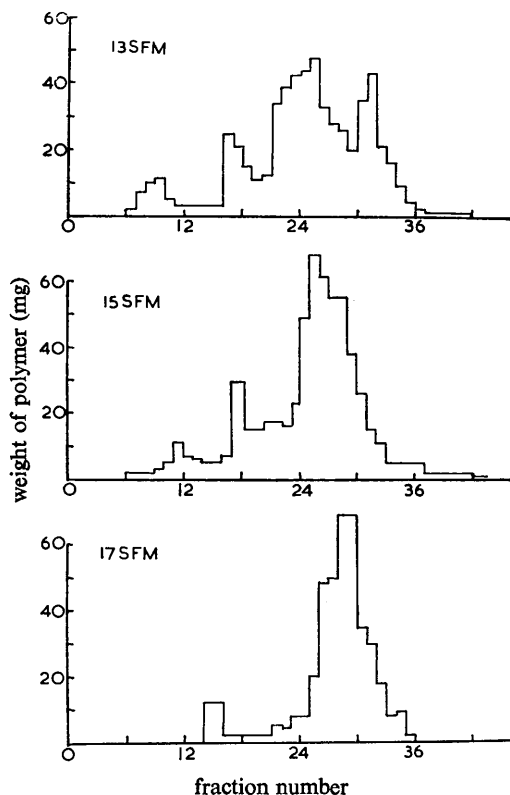


FIG. 4.—Weights of block copolymer fractions recovered from the column.

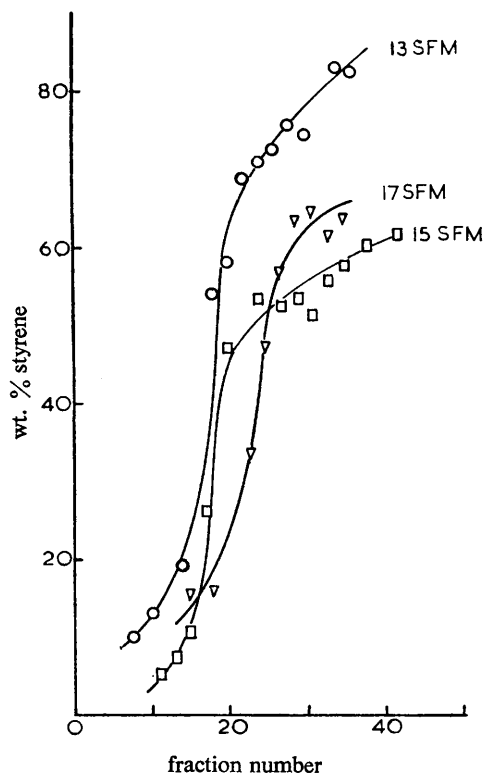


FIG. 5.—Compositions of block copolymer fractions recovered from the column.

In fig. 5, the percentage by weight of styrene is shown plotted against the serial number of the fraction collected for the three column fractionations referred to in table 6. This figure should be examined in conjunction with the histograms in fig. 4.

DISCUSSION

It is the purpose of this section to consider critically whether a block copolymer of known molecular structure has been prepared and how far this has been separated into a series of fractions homogeneous with respect to molecular weight and chemical composition.

The first stage of the synthesis was the preparation of linear polystyrene chains each with a single hydroperoxy end-group. The success of this operation depended first upon the mode of break-down into radicals of the dihydroperoxide initiator and the actual chain-initiating process, and secondly upon the chain-terminating process since the nature of the end-groups was determined by these steps. The presence in

the product of polystyrene with no hydroperoxy end-groups would not present a serious difficulty since such inactive polymer was removed as homo-polystyrene in the preliminary fractionation of the block polymer. The presence of some polystyrene with a hydroperoxy group at each end of the molecule, such as might arise from the mutual termination of growing chains by combination, would be more undesirable. If both end-groups were attacked by ferrous ions in the second stage of the synthesis then block polymer of the sandwich type,



would be produced as well as the required simple binary copolymer,

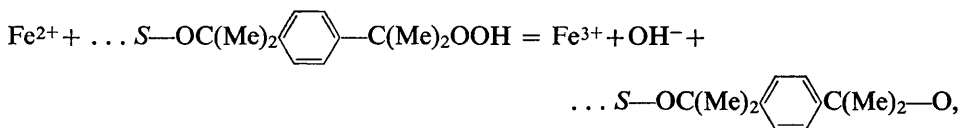


where M represents methyl methacrylate and S styrene. These two types of polymer could not readily be separated by solvent elution.

The mechanism of the bulk polymerization of styrene using the same dihydroperoxy initiator has been discussed at length by Molyneux.¹³ He concluded that, at the temperature and catalyst concentration used in this work and at low degrees of monomer conversion, the average number of hydroperoxy groups in a chain was unity. If bimolecular coupling of growing chains were the main termination process 50 % of polymer molecules would have one hydroperoxy end-group, 25 % two and 25 % none; whereas if chain termination occurred mainly by transfer to initiator then all the polymer molecules would have one hydroperoxy end-group. Thus, it may safely be concluded that more than half of the polystyrene molecules have one hydroperoxy group and less than a quarter have two.

Subsequently this polystyrene was divided into fractions having narrow ranges of molecular weights. In the process the highest molecular weight material was discarded; this included predominantly the polymer formed by mutual combination of growing radicals since this had a higher average molecular weight than chains terminated by transfer. Thus, the polystyrene fraction used for the second stage of the synthesis was composed principally of molecules with a single hydroperoxy end-group and probably not more than 10 % had two hydroperoxy end-groups.

This polystyrene was completely dissolved in monomeric methyl methacrylate and constituted the disperse phase in the emulsion polymerization. Any copolymer obtained therefore could not have a random structure but must be either a block or a graft. Trial experiments in which the hydroperoxy-ended polystyrene was omitted from the recipe, all the other components being included as in table 4, showed effectively no polymerization of the methyl methacrylate. Thus, polymerization in normal runs was initiated only by attack of ferrous ions in the dispersion medium on the hydroperoxy groups of the polystyrene, presumably at the interface between the emulsion droplets and the surrounding medium. This goes according to the equation,



where the last species on the right-hand side is a radical attached to a polystyrene chain ($\dots \text{S}$) and is capable of initiating polymerization of the methyl methacrylate.

The product must therefore have contained polystyrene and polymethyl methacrylate chains coupled end-to-end. The full details of the molecular structure of this polymer were controlled by the nature of the chain-terminating processes for the methyl methacrylate polymerization.

If chains were terminated by transfer to monomer then appreciable quantities of methyl methacrylate homo-polymer would have been produced by secondary propagation from the radicals formed. As the preliminary fractionation data showed, this was not found. As the concentration of polymer by weight in the emulsion droplets never exceeded 5 %, transfer to polymer was unlikely to be important. Mutual termination of growing chains was therefore the main mechanism and for methyl methacrylate this has generally been believed to occur largely by disproportionation.¹⁴ This was supported by the observation (table 7) that the copolymer compositions calculated from the molecular weights, assuming only one polystyrene block per molecule, were in agreement with those obtained by u.-v. absorption measurements. Termination by combination would have led to two polystyrene blocks per molecule and a much higher molecular weight for the same chemical composition.

It may be deduced from the data on the preliminary fractionation of the copolymer (table 5) that about one half of the polystyrene has been involved in copolymer formation during the time allowed for the emulsion polymerization. Thus, assuming 10 % of the polystyrene had two hydroperoxy end-groups, only 5 % of the block copolymer would be expected to have the sandwich structure, with a polystyrene segment between two methyl methacrylate segments, and 95 % should consist of the simple binary structure as required.

The effectiveness of the column fractionation depended upon the factors affecting the solubility of the copolymer in the mixture of solvent and non-solvent. The two main factors were molecular weight and chemical composition. If the polystyrene fraction used to prepare the copolymer had been of absolutely uniform chain length then the molecular weight and chemical composition would have been uniquely related to one another for each copolymer molecule and the solubilities would have been controlled by a single parameter. However, the polystyrene was subjected only to a single-stage fractionation as fairly large samples were required to give a reasonable yield of copolymer. Thus, it must have contained material with some degree of chain length dispersity. This fact had an important bearing on the success of the elution-column separation.

There are two basic classes of non-solvent which might be used in combination with any given solvent. The first is a non-solvent which is a more powerful precipitant for the secondary polymer (methyl methacrylate) than for the primary one, for example, petrol ether. The second class of non-solvent is a more powerful precipitant for the primary polymer (styrene), for example, methanol. These two systems should act quite differently and a consideration of their expected properties shows why the second approach was used here.

In the first system, as the solvent content of the liquid flowing down the column steadily increases the first polymer to dissolve contains the shortest chains of the primary polymer with the least secondary polymer attached, i.e., the lowest molecular weight material with the highest weight fraction of primary polymer. In later fractions, some of the higher molecular weight primary polymer with a very low weight fraction of secondary polymer and also the shorter chain primary polymer with a fairly high weight fraction of secondary polymer dissolve together. Thus, the copolymer fractions tend to have a rather sharp molecular weight distribution (sharper probably than the initial primary polymer) but a broad chemical composition distribution.

In the second system, the presence of a block of the more soluble secondary polymer attached to the primary polymer has the effect of increasing its solubility at a particular solvent/non-solvent ratio to an extent related to the weight fraction

of the secondary polymer. However, for a given primary chain, this weight fraction can only be increased by increasing the molecular weight of the whole molecule. This has the effect of decreasing its solubility. Thus the two factors, chemical composition and molecular weight, act in opposition.

Fig. 6 shows schematically the volume fraction of solvent in the liquid mixture which will just dissolve a molecule plotted against the weight fraction of primary polymer in the molecule for three values of the chain length P of the primary chain, $P_1 < P_2 < P_3$. As chemical composition is in general more important than molecular weight in determining solubility, the minima in the curves will lie, as shown, at small values of x . Early fractions collected from the column, such as the one enclosed between the

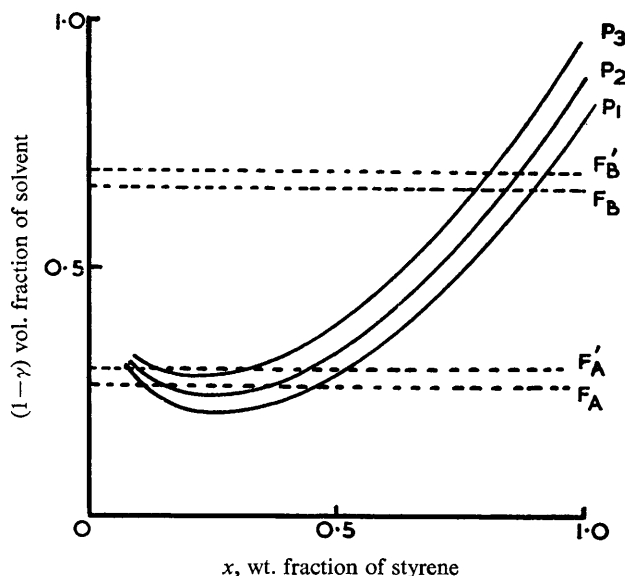


FIG. 6.—Schematic representation of block copolymer solubility as a function of composition.

lines F_A and F'_A , quickly remove all the copolymer bearing very long secondary polymer blocks especially where this is associated with a short primary block. Later fractions, such as F_B and F'_B , have a progressively increasing weight fraction x of primary polymer. Generally speaking, the breadth of the distribution of x in any fraction should be comparable with the breadth of distribution of chain length in primary polymer since for the benzene + methanol system total dissolution occurs over the solvent volume fraction range 0.25–0.75.

Thus, the use here of a non-solvent which acted mainly against the primary polymer, styrene, maintained a sharp distribution in the chemical composition of the copolymer fractions since the primary polymer was itself well fractionated. The molecular weight distribution of the copolymer fractions was probably a little broader than in the primary polymer but this was a minor disadvantage.

The correspondence between this predicted behaviour and the experimental results from the fractionating column may be judged from fig. 5. For batch 15SFM, the gauze compartment was not heated and it is seen that the separation in the later fractions was inferior to that obtained for batch 13SFM which started with the same non-solvent mixture. Fractions of the same composition also came later in 15SFM than in 13SFM as the volume fraction of solvent required to dissolve a

given composition was higher at the lower temperature. Batch 13SFM shows that a satisfactory separation into narrow bands of the bulk of the copolymer in the intermediate composition range was achieved. The curvature of the plots was due to the fact that the solvent content of the liquid increased roughly with the logarithm of the fraction number so that later fractions were taken over narrower liquid composition intervals. The scatter of the points, especially towards the ends of the runs, was probably due to minute pieces of highly swollen gel becoming detached from the gauze and carried down the column without being dissolved. The separation of 17SFM ran parallel with 13SFM but equivalent compositions in 17SFM came later as the column was set up with pure methanol as non-solvent instead of with 80 % methanol + 20 % benzene as for 13SFM. This gave a clearer separation of the early fractions which contained a large amount of methyl methacrylate but showed no advantage in the intermediate composition range.

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