

SAN Copolymer by Suspension Polymerization. II.

Bead Size Distribution and Molecular Weight

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Synopsis

Beads of SAN copolymer produced by suspension polymerization have sizes distributed over the range of 0.2–3.0 mm; 70%–80% of these are in the range of 0.4–0.8 mm diameter. Studies on molecular weight and molecular weight distribution showed that the average molecular weight of the polymer was higher with increasing sizes of beads. Fractionation of small-, medium-, and large-sized beads as well as determination of molecular weight by GPC provided clear evidence that there is also an increase of polydispersity and higher molecular weight ends with increasing diameter of beads. This increase in molecular weight and polydispersity in larger beads is probably due to slow thermal polymerization in near absence of initiator toward the end of polymerization.

INTRODUCTION

Particles of different sizes, from $10\ \mu$ (1×10^{-3} cm) to 3–4 mm in diameters, in the form of pearls or beads are obtained from suspension polymerization in aqueous medium, in contrast to particles of emulsion polymers which are less than $1\ \mu$ in diameter.¹ These particles are formed from the monomer droplets kept in suspension by stabilizers and chosen properties of the suspension medium under the operating conditions. At the initial stage, the droplets undergo constant changes in size and shape with progress in polymerization, transforming finally through semisolid to solid beads. It is therefore natural that beads of different sizes are obtained in the final polymer product. In commercial practice for styrene polymers, beads of narrow size ranges are desired; above 80% of the beads should be retained on a sieve of aperture 0.4 mm (40 mesh sieve) or at the most on a sieve of aperture 0.25 mm (60 mesh).² Beads of diameters greater than 2 mm and less than 0.177 (80 mesh) are not desired, except, of course, those used for expanded polystyrene³ for problems relating to storage, handling, extrusion, and the like.

However, beads of smaller and larger diameters beyond these desired ranges are often formed during polymerization. It is probable that the mass of monomer in the different sizes of particles in suspension might encounter slightly different reaction conditions during the reaction period for a batch, particularly at later stages of polymerization; these may, for example, be the variations in monomer concentrations or relating to heat and mass transfer. These would lead to different molecular weights in the beads. It was of interest therefore to examine whether any variation in molecular weight and molecular weight distribution appears in different sizes of polymer beads and, if so, to what extent. This study was carried out with styrene–acrylonitrile (SAN) copolymer produced by suspension polymerization.

EXPERIMENTAL

The SAN copolymer was produced by suspension polymerization in aqueous medium using suspension stabilizers, initiator, etc. in a 30-l reactor unit. Polymerization was carried out to completion. After cooling, the polymer beads were separated in a centrifuge, washed thoroughly with water, and dried under vacuum at 45–50°C. The acrylonitrile feed was above the azeotropic composition; the polymer product contained about 26% acrylonitrile, and detailed analysis showed it to be chemically homogeneous.⁴ The dried beads were sieved into different sizes; the sieve analysis and the corresponding average molecular weights of each size range of beads are given in Table I.

Three ranges of beads, two coarser (2.0–3.36 mm and 0.8–2.0 mm in diameter) and one smaller (0.40–0.50 mm in diameter), the latter constituting the major part of product, were chosen for detailed study. Each of these were then fractionated. The beads were dissolved in methyl ethyl ketone to make a 1% solution, and the solution was kept in a thermostated bath at 25°C for about 2 hr. A controlled amount of methanol (at 25°C) was then added gradually when turbidity appeared due to the separation of polymer fractions, and the flask was left undisturbed in the bath for about 7 hr for the polymer to settle down. The solution was decanted and an additional amount of methanol was added to obtain the next fraction of the polymer. Seven to nine such fractions were thus separated from each size range of the beads, dried under vacuum at 45–50°C, and weighed, and the molecular weights of the fractions were determined. The average molecular weight (\bar{M}_w) was determined by viscometry using the reported values of K and α .⁵

RESULTS AND DISCUSSIONS

The results of fractionation and the \bar{M}_w of each fraction of the three bead sizes are given in Table II. The cumulative weight percent of the fractions, $I(M)$, for each bead size was calculated by the normal procedure⁶ of taking $I(M)$ for the n th fraction as the sum of all the fractions lower than the n th fraction plus half of the n th fraction. The integral distribution curves between $I(M)$ and \bar{M}_w are given in Figure 1. The differential distribution curves are given in Figure 2.

Fractionation of polymers by solvent/nonsolvent system has the limitation that when applied to several polymer samples, even though the same procedure is followed, the corresponding fractions are not strictly comparable in \bar{M}_w . However, their distribution curves indicate the patterns of molecular weight distribution, and these can be seen from Figures 1 and 2.

TABLE I
Sieve Analysis and Molecular Weights of the SAN Polymer Beads

Sample	Sieve size, mm	Wt.-% of size range	Av. mol. wt. \bar{M}_w	Statistical av. mol. wt. \bar{M}_w
A	larger than 3.36	nil	—	—
B	2.0–3.36	3.5	330,000	350,000
C	0.8–2.0	15.0	280,000	303,000
D	0.5–0.8	14.0	270,000	275,000
E	0.4–0.5	65.0	250,000	265,000
F	smaller than 0.4	2.5	—	—
	Beads (unsieved)	—	260,000	275,000

TABLE II
Cumulative Weight and Molecular Weight of Fractions of Different Bead Sizes

Sample	Fraction no.	Wt-% of polymer bead	Cumulative wt-% $I(M)$	Av. mol. wt. \bar{M}_w
B	1/1	6.0	94.6	864,000
	1/2	1.8	90.0	650,000
	1/3	6.9	85.65	598,000
	1/4	7.0	78.7	505,000
	1/5	20.8	64.8	400,000
	1/6	16.9	45.95	305,000
	1/7	16.3	29.35	250,000
	1/8	10.2	16.1	176,000
	1/9	11.0	5.5	57,000
C	2/1	10.0	93.2	742,000
	2/2	7.0	84.7	515,000
	2/3	5.6	78.3	440,000
	2/4	18.0	66.5	370,000
	2/5	3.6	55.7	281,000
	2/6	30.0	38.9	220,000
	2/7	3.8	22.0	136,000
	2/8	20.1	10.05	81,000
E	3/1	12.0	92.55	542,000
	3/2	14.1	79.5	400,000
	3/3	13.4	65.3	310,000
	3/4	18.2	49.5	230,000
	3/5	14.4	33.2	190,000
	3/6	12.0	20.0	140,000
	3/7	14.0	7.0	80,000

The data in Table I show clearly that the larger the bead size, the higher was the average molecular weight, so much so that the average molecular weight of the beads of size 2.0–2.36 mm was about 32% higher than that of the beads of 0.40–0.50 mm range, which constituted the bulk of this product (65%). These values of the average molecular weight of different size ranges seem to be fairly

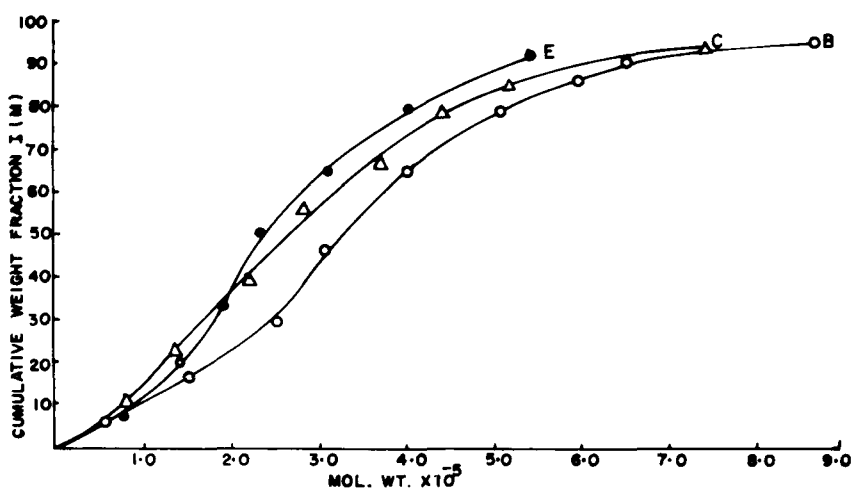


Fig. 1. Integral distribution curves of SAN polymer beads: B, bead size 2.0–3.36 mm; C, bead size 0.8–2.0 mm; E, bead size 0.4–0.5 mm.

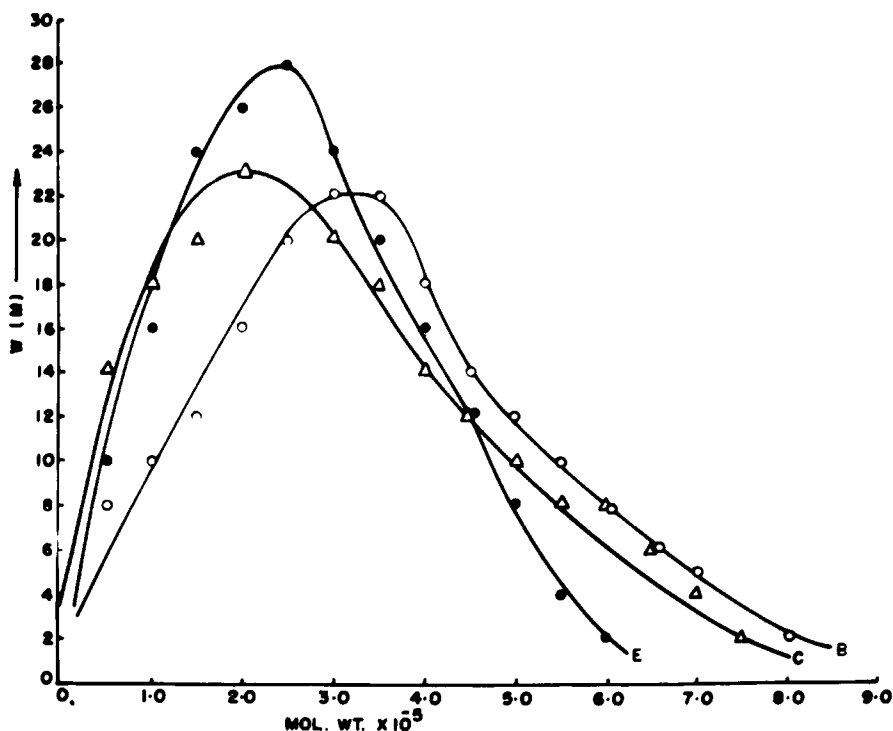


Fig. 2. Differential distribution curves of SAN polymer beads: B, bead size 2.0–3.36 mm; C, bead size 0.8–2.0 mm; E, bead size 0.4–0.5 mm.

accurate within the limitations of the viscometry method since the statistical \bar{M}_w calculated from the actual weight of each sizes and their respective \bar{M}_w agree closely with the \bar{M}_w of the total polymer product as shown at the bottom of Table I. Similarly, the statistical \bar{M}_w for each bead sizes calculated from the fractions obtained and their corresponding \bar{M}_w were also close, within 10% of the \bar{M}_w of the unfractionated beads.

The results in Table II also qualitatively show that the larger the bead size, (a) the wider is the spread of molecular weights and (b) the higher is the \bar{M}_w of the first fraction. These can also be clearly seen from the distribution curves in Figures 1 and 2. An accurate quantification of the molecular weight spread with increasing bead sizes from these data may not be correct because of the limitation of fractionation, but comparison based on relative values reveal an acceptable picture.

Standard deviations (S.D.) indicate the accuracy of analysis of samples of the same composition; hence, when the analysis is carried out with the same accuracy, wide variations in the S.D. would result only from changes in composition. Similarly, the average molecular weights (\bar{M}_w or \bar{M}_n) of samples of a polymer from the same batch should show S.D. values related to the representative molecular weight within an acceptable limit. If the S.D. is much higher, it would indicate that molecular weight distribution is different or polydispersity is higher. The S.D. in molecular weights, calculated by the usual formula showed that the S.D. between sieved beads and unsieved beads was about 46,000. For the molecular weights of the fractions from the respective bead sizes with respect to the \bar{M}_w of the unfractionated beads, the S.D. values were about 269,000 for sample

B, 229,000 for sample C, and 161,000 for sample E. This added further evidence that the polydispersity was higher with increasing bead sizes.

$$\text{S.D.} = \sqrt{\frac{\sum_{i=1}^n (M_i - \bar{M}_w)^2}{n - 1}}$$

An attempt was then made to qualitatively assess the polydispersities of the beads from the cumulative weight percentage and the differential weight percentage.⁷ Using the weight-average values of Table II, the calculated values of \bar{M}_w/\bar{M}_n , although showing a tendency to decrease with bead sizes, were lower than 2, which appeared to be unacceptable. Hence, direct measurement of polydispersity was made by gel permeation chromatography. The SAN product obtained from another experiment in the same apparatus was sieved, and the molecular weights were determined using columns packed with polystyrene gel. This SAN product contained more larger beads. The results are given in Table III. These results clearly showed that the polydispersity was higher with increasing bead sizes; the value was 2.79 for 0.4–0.5 mm beads whereas it was 3.68 for 2.0–3.36 mm beads. Thus, the difference in polydispersities in the small and large beads was considerable.

Evidently, this higher polydispersity resulted from the formation of more higher molecular weight polymer molecules in the larger-sized beads. With increasing bead size, the molecular weights of the trailings also become higher and higher (Fig. 2). Plots of apparent $\bar{M}_w(\text{maximum})/\bar{M}_w(\text{minimum})$, average molecular weights, or the polydispersity data (Table III) against mean bead sizes shown in Figure 3 all show a similar trend of rising with higher bead size.

The formation of higher molecular weight polymers with increasing bead size could be the result of one or more of several factors. With increasing bead size, the surface-to-volume ratio of the reacting mass in a globule decreases, which would adversely affect the transfer of exothermic heat. This could lead to localized higher temperature inside the globule/bead which would tend to give lower molecular weight products. On the other hand, due to turbulent motions, the globules containing the monomer fluid undergo constant peripheral distortions and renewal of surfaces which would offset the above conditions. In fact, the formation of higher molecular weight polymers in the larger beads indicates that the transfer of heat is satisfactory and thermal conditions in the beads are not playing an important role.

It is more probable that kinetic factors and the history of progress of poly-

TABLE III
Polydispersity in Different Bead Sizes Measured by GPC

Sieved fraction	Bead sizes	wt-% of sample	polydispersity \bar{M}_w/\bar{M}_n
I	2.0–3.36	43.5	3.68
II	0.8–2.0	49.0	3.37
III	0.5–0.8	3.2	2.92
IV	0.4–0.5	3.0	2.79
Unsieved beads	—	—	3.48

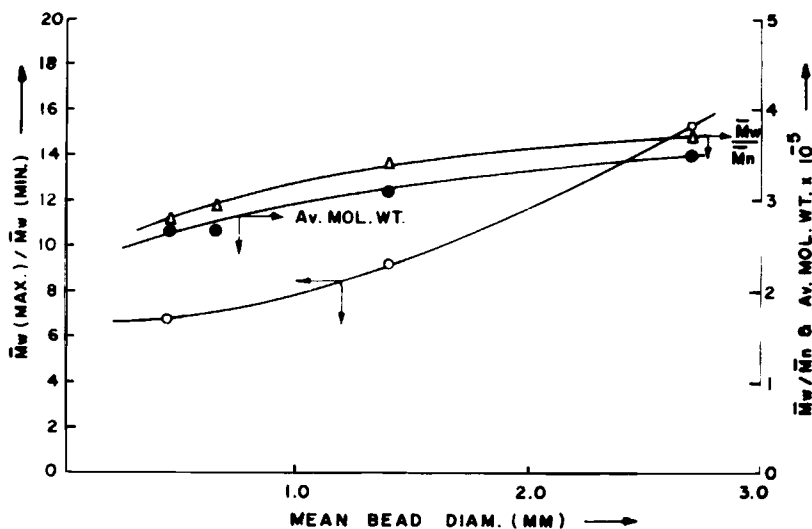


Fig. 3. Effect of $\bar{M}_w(\text{max})/\bar{M}_w(\text{min})$, \bar{M}_w/\bar{M}_n , and \bar{M}_w on bead size.

merization is predominantly responsible for the spread toward higher molecular weights. With progress of polymerization, it is possible that more of the monomer present in the larger globules will contribute toward larger chain growth. This is reflected through the shift of the differential distribution curves toward the higher molecular weight side in larger beads.

Increase of highest molecular weight ends with increasing bead size probably appears toward the end of the polymerization. The initiator concentration in the beginning was 0.085 g-mole/l of monomer. After the polymerization had progressed for about 9 hr and the conversion had reached 85%, the initiator concentration would have dropped down to 0.0011 g-mole/l according to the relationship

$$[I] = [I_0] e^{-kt}$$

assuming that the initiator efficiency was unity and all the free radicals formed were utilized in initiating the polymerization. At this stage the temperature of polymerization was raised by 10°C for completion of polymerization. The semisolid beads will have very high viscosity, and the diffusion of monomers remaining in between the polymer chains to the growing chain radicals would be retarded. The polymerization would also be predominantly thermal and slow due to almost complete depletion of initiator. The mercaptan used for chain termination would also be completely consumed. All these factors will facilitate the formation of much higher molecular weight chains. The effects of these factors would be more pronounced in the larger beads which would then contain comparatively more of the highest molecular weight end products.

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