Particle Size Control in Emulsions of Hydrocarbon Soluble Polymers

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SYNOPSIS

Hydrocarbon solutions of polybutadiene, polyisoprene, and polystyrene may be converted into emulsions. The hydrocarbon solvent may then be removed by distillation. The molecular weight of the polymer controls the particle size of its emulsion. An increase in polymer molecular weight causes an increase in the particle size of its emulsion.

INTRODUCTION

Many investigators have converted hydrocarbon solutions of rubbers into emulsions.[1-10] For example, Preiss, Endwell, and Simpson[1] converted a hydrocarbon solution of *cis*-polyisoprene into a *cis*-polyisoprene emulsion. This was accomplished by intimately mixing the hydrocarbon solution of polyisoprene with water containing an emulsifier. A homogenizer or colloid mill was used in this step. The hydrocarbon solvent was removed from the emulsion by distillation. Brodkey et al.,[5] converted a butyl rubber–solvent mixture into an emulsion by mixing with an aqueous solution of an organic sulfate emulsifier and a monovalent salt of dihydrogen ortho-phosphate. The solvent was distilled from the emulsion.

Analogous techniques have been used to prepare emulsions of ethylene–propylene rubber, ethylene–propylene–terpolymer rubber, polybutadiene rubber, and SBR rubber.

In some cases the particle size of these emulsions was determined by electron microscopy. However, in no case was the effect of polymer molecular weight on emulsion particle size examined.

This paper discusses the effect of polymer molecular weight on the particle size of emulsions of polybutadiene, polyisoprene, and polystyrene. Increasing the molecular weight of the polymer increases the particle size of the emulsion. The emulsions are prepared by mixing a solution of the polymer with water containing an emulsifier followed by distillation of the solvent.

EXPERIMENTAL

Polybutadiene, polyisoprene, and polystyrene were prepared by the secondary butyllithium initiated polymerization of the appropriate monomer in cyclohexane.[11] Infrared analysis showed the microstructure of the polybutadienes to contain 43% *cis*-1,4, 49% *trans*-1,4, and 8% 1,2 structure. The polyisoprene was predominately *cis*-1,4.

Polybutadiene, 25,000 MW, 20.0 g, was dissolved in 400 g of toluene. This solution was added to a stirring solution of 4.4 g of Dresinate-731 (purchased

Table I Latex Particle Size as a Function of Polybutadiene Molecular Weight[a]

Entry	Molecular Weigh $\times 10^{-3}$	Particle Size (μ) ($D\bar{n}$)	$D\bar{w}/D\bar{n}$	% Solids
1	31	.105	3.1	4
2	38	.122	5.4	4
3	80	.173	4.7	4
4	90	.221	3.4	4
5	105	.357	2.8	6

[a] 22% Dresinate-731, based on polybutadiene.

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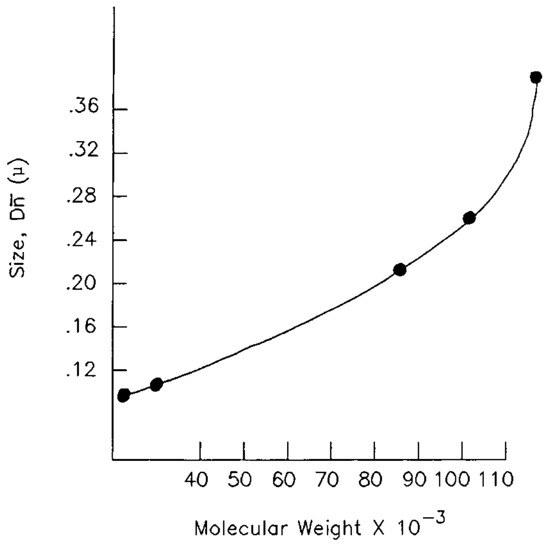

Figure 1 Latex particle size as a function of polybutadiene molecular weight.

from Hercules) in 400 g of water in a Waring blender. Mixing was continued for 5 min. This mixture was passed twice through a Manton-Gaulin

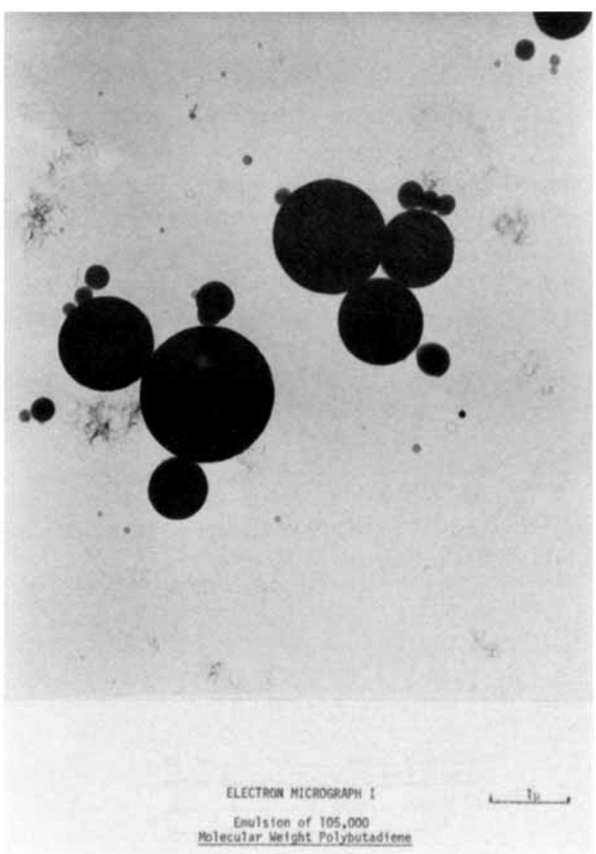

Figure 2 Emulsion of 105,000 MW polybutadiene.

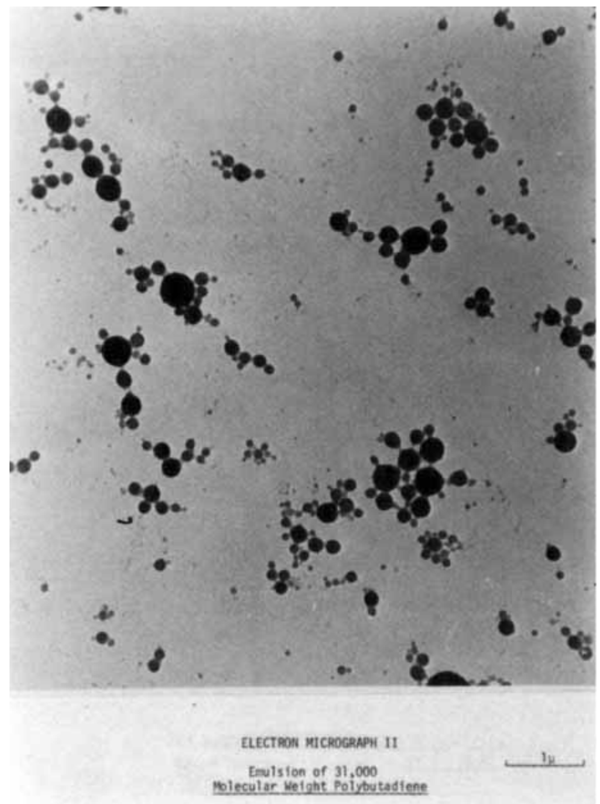

Figure 3 Emulsion of 31,000 MW polybutadiene.

Model 15 M-8TA lab homogenizer with 7000 pounds pressure on the first stage and 1000 pounds on the second stage. The toluene was removed by distillation at atmospheric pressure. The emulsion was filtered through cheese cloth to remove any coagulum. The rubber concentration of the final emulsion was determined, 4.8%, from which the percent agglomeration was determined at 4%.

A Phillips EM 100B electron microscope was used to determine particle size. Particle sizes were measured visually and with a Carl Zeiss particle size analyzer TGZ-3.

Table II Polybutadiene Emulsion Particle Size as a Function of Concentration in Toluene[a]

$MW \times 10^{-3}$	Particle Size, $D\bar{n}$ (μ)	$D\bar{w}/D\bar{n}$	% Solids in Toluene
31	.105	3.1	4
26	.0603	—	17
26	.0877	4.6	26

[a] Twenty-two percent Dresinate-731, based upon polybutadiene.

RESULTS AND DISCUSSION

The polymer emulsions were prepared from hydrocarbon solutions of polymers as described in the Experimental section. The particle sizes of the emulsions were determined with the aid of a Phillips EM 100B electron microscope. The polymers examined were polybutadiene, polyisoprene, and polystyrene.

The molecular weight of polybutadiene controls the particle size of its emulsion (Table I). The polymer concentration in the emulsion was held constant at 4–6% and the concentration of emulsifier, Dresinate-731, was kept at 22% based upon polybutadiene. A toluene solution of 31,000 MW polybutadiene was converted into an emulsion, which, after distillation of the toluene, had a diameter number average particle size of 0.105 μ, entry 1. As the MW is increased to 38,000, 80,000, 90,000, and 105,000 an increase in particle size is noted with 0.357 μ diameter number average particle size ($D\bar{n}$) occurring at 105,000 MW. The distribution of particle

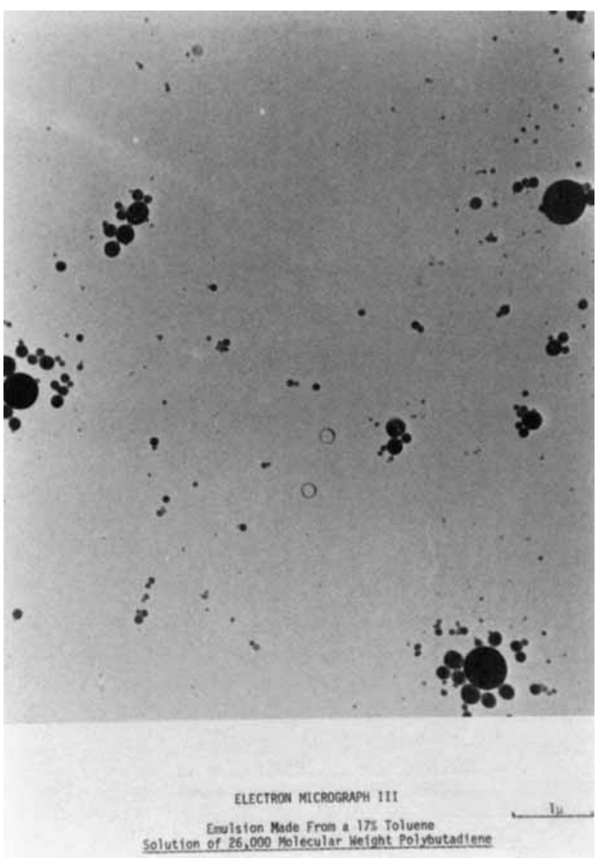

Figure 4 Emulsion made from a 17% toluene solution of 26,000 MW polybutadiene.

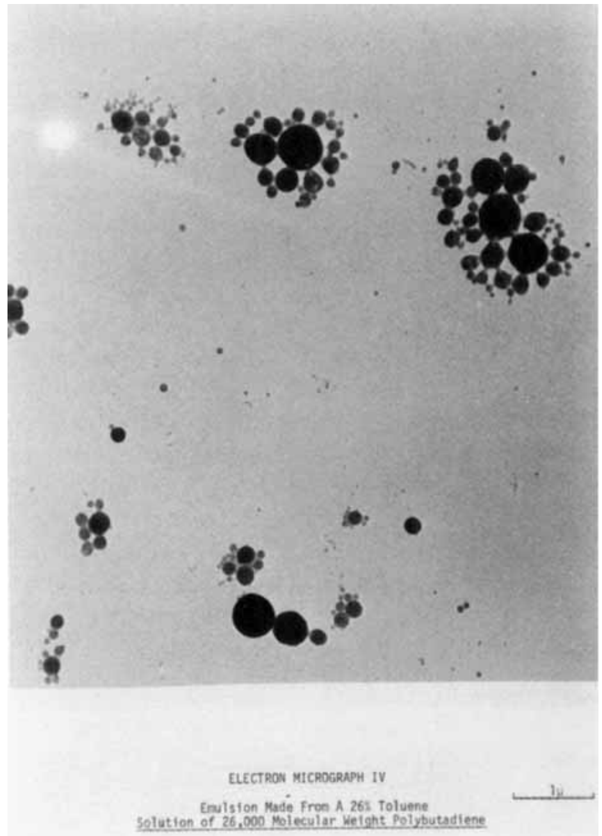

Figure 5 Emulsion made from a 26% toluene solution of 26,000 MW polybutadiene.

size is large as indicated by large uniformity indices ($D\bar{w}/D\bar{n}$), 2.8–5.4. A correlation does not exist between polybutadiene molecular weight and uniformity index. In each case about 900 particles were visually counted.

Figure 1 is a graphical presentation of the data of Table I. Using this curve a desired emulsion particle size may be formed merely by choosing the appropriate polybutadiene molecular weight. This precise control of the particle size of emulsions has theretofore never been achieved.

No polymer degradation occurs during Manton–Gaulin treatment. Polybutadiene, 105,000 MW, passed through the Manton–Gaulin five times showed negligible viscosity change. Initial $\eta sp/c = 1.35$, in toluene at 25°C, 0.1 g/dL. Final $\eta sp/c = 1.21$.

The increased particle size at 105,000 molecular weight compared to 31,000 MW is controlled by molecular weight alone and does not result from an increased solution viscosity of 105,000 MW polybutadiene. In fact, a 26,000 MW polybutadiene at 26% solids in toluene has a viscosity of 216 Hz while a 105,000 MW polybutadiene at 6% solids has a solution viscosity of 56 Hz. The particle sizes are 0.0877 μ and 0.357 μ, respectively.

Figures 2 and 3 visually show this effect. Large particles are formed from the hydrocarbon solution of 105,000 MW polybutadiene while small particles are formed with 31,000 MW polybutadiene.

The concentration of polybutadiene in its hydrocarbon solution and thus the concentration of the emulsion has a slight effect on the particle size of the emulsion (Table II). At a constant MW of 26,000–31,000, the particle size was examined at three concentrations, 4%, 17%, and 26%. The particle size decreases from 0.105 μ to 0.0877 μ over this 6.25-fold increases in concentration. The large uniformity indices indicate a broad distribution of particle sizes. Figures 4 and 5 visually show this effect. The effect of polybutadiene concentration in hydrocarbon solvent on emulsion particle size is not nearly as great as the effect of polybutadiene molecular weight on emulsion particle size.

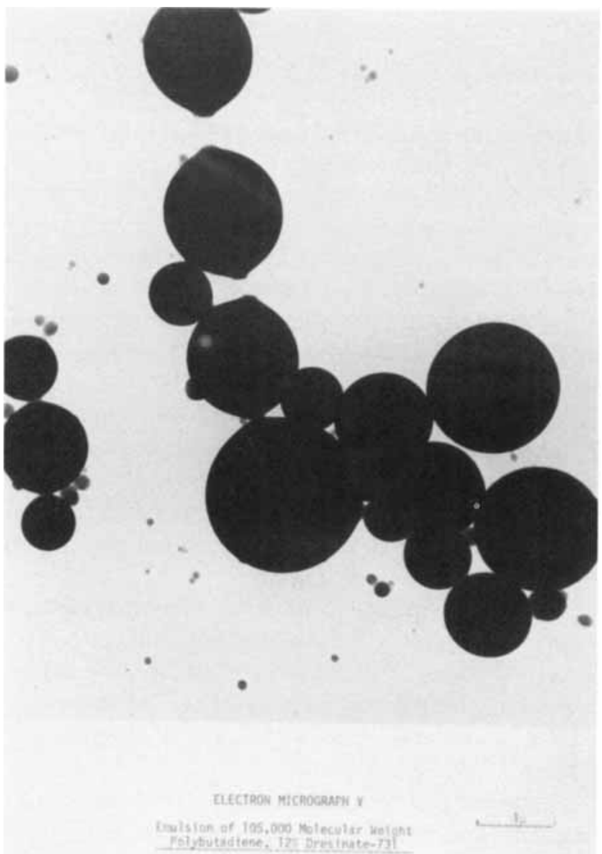

Figure 6 Emulsion of 105,000 MW polybutadiene, 12% dresinate-731.

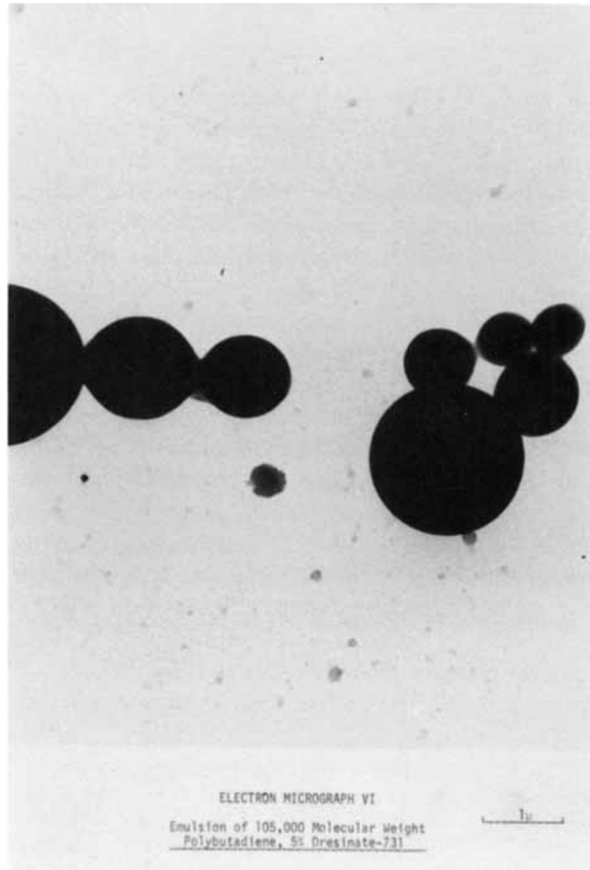

Figure 7 Emulsion of 105,000 MW polybutadiene, 5% dresinate-731.

The experimental data presented in Tables I and II and Figures 2–5 were carried out at a constant emulsifier concentration of 22% based upon rubber, Dresinate-731. The effect of emulsifier concentration on particle size has been determined. Besides 22% Dresinate, emulsions of polybutadiene, were prepared at emulsifier concentrations of 12%, 5%, and 1%. The initial rubber concentration was 23%. The polybutadiene MW was held constant at 105,000. At Dresinate-731 levels lower than 22%, significant rubber agglomeration occurs during the solvent stripping step so that the final latex concentrations were 18%, 15%, and 6%. Figures 2, 6, 7, and 8 show that the emulsifier level does not effect the particle size of the emulsion. However, this may reflect the increased agglomeration of certain particle sizes.

The effect of molecular weight on emulsion particle size occurs with polymers other than polybutadiene. Polyisoprene and polystyrene also exhibit this effect.

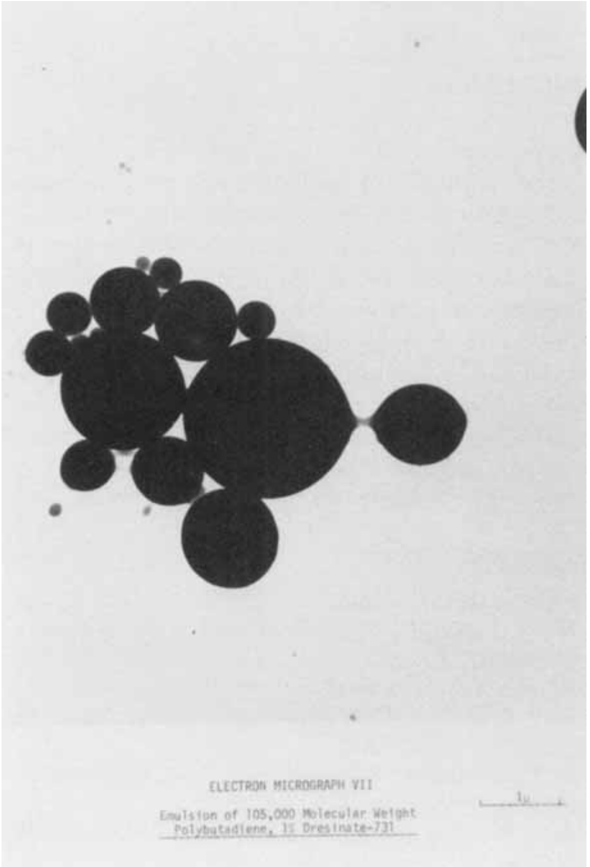

Figure 8 Emulsion of 105,000 MW polybutadiene, 1% dresinate-731.

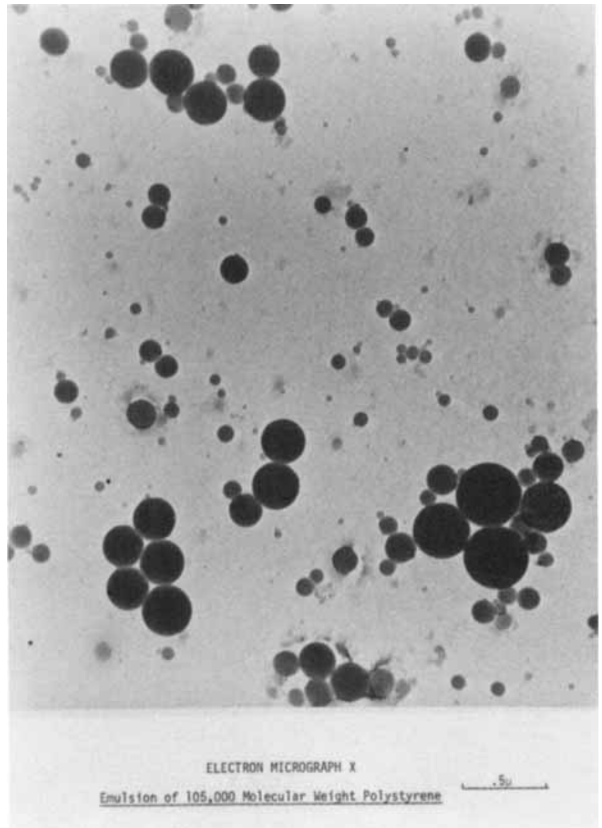

Figure 10 Emulsion of 24,000 MW polyisoprene.

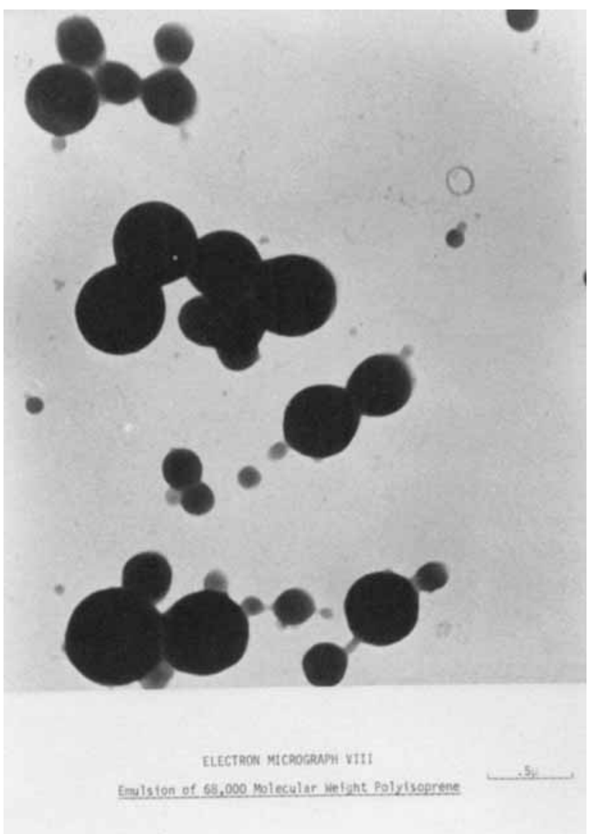

Figure 9 Emulsion of 68,000 MW polyisoprene.

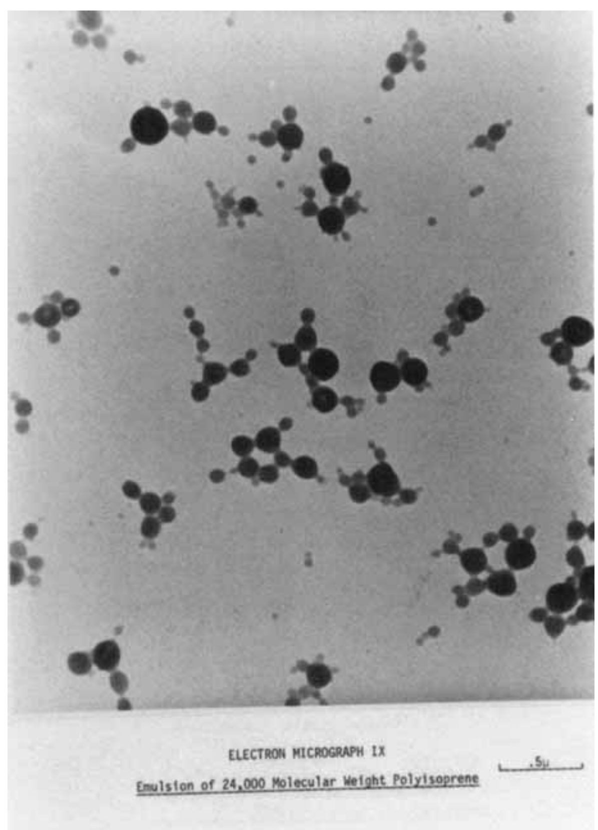

Figure 11 Emulsion of 105,000 MW polystyrene.

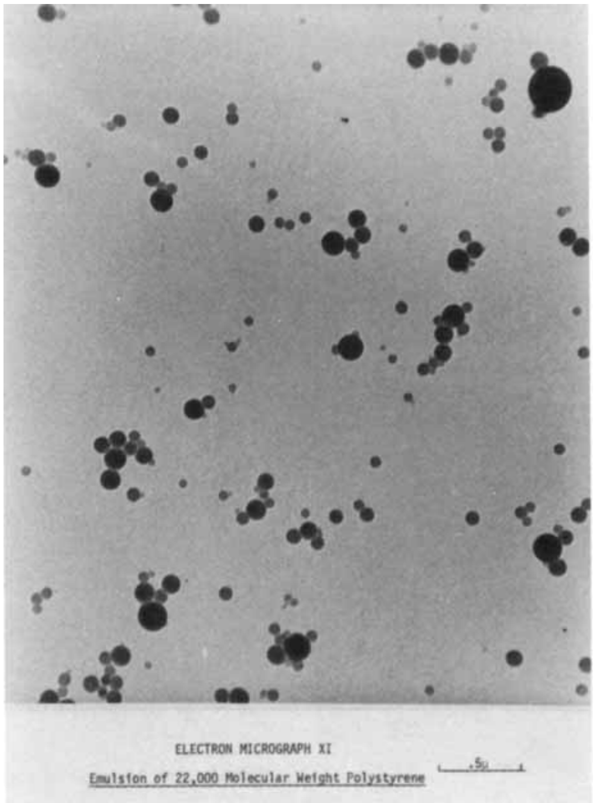

Figure 12 Emulsion of 22,000 MW polystyrene.

Polyisoprene of 68,000 molecular weight has a number average particle size of 0.89 μ with a large distribution of particle sizes (uniformity index 2.5) (Fig. 9). A lower molecular weight, 24,000, results in much smaller particles, 0.13 μ, $D\bar{w}/D\bar{n} = 3.3$ (Fig. 10).

Polystyrene also shows this effect (Figs. 11 and 12). Relative to 105,000 MW polystyrene, 22,000 MW polystyrene gives small particle size latices.

CONCLUSION

The work presented in this paper shows that hydrocarbon solutions of polybutadiene, polyisoprene, and polystyrene can be converted into emulsions with no solvent present. The molecular weight of the polymer dissolved in the hydrocarbon solvent determines the particle size of the solvent-stripped emulsion. An increase in the molecular weight of the polymer causes an increase in the particle size of its emulsion. This technique enables the precise control of emulsion particle size which has heretofore in this manner never been achieved.

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