

The Ultrafiltration of Solutions of Polymers Containing Microgel

M. R. AMBLER, *Chemical Development Services, The Goodyear Tire and Rubber Company, Akron, Ohio 44308*

Synopsis

The use of ultrafiltration in determining microgel contents of synthetic rubbers containing high levels of microgel was extensively studied. From experiments with a nonagitated filtration cell, it was found that accurate microgel contents could be obtained only when concentration polarization of the membrane was disallowed. GPC studies of the filtrates indicated that changes in the molecular weight distribution of the filtered polymer occurred as a result of the occurrence of concentration polarization. The use of an agitated filtration cell was found to inhibit the occurrence of concentration polarization, allowing the proper filtration of larger volumes and higher concentrations of solutions of these types of polymers.

INTRODUCTION

The filtration of polymer solutions has proved to be an effective means of separating microgel particles from soluble polymer molecules.¹ Under ideal conditions, total separation of microgel, those particles which will not pass through the membrane (retentate), and soluble polymer, which will normally pass through the membrane (permeate), will be accomplished. However, recent work in the field of reverse osmosis technology has shown that "ideal" conditions are sometimes hard to achieve and complete and total separation of retentate and permeate is not achieved.² This has also been observed with synthetic polymer solutions.^{3,4}

In our laboratories, an ultrafiltration test to determine microgel content has been in use for several years. In this period of time, we have observed several things that occur frequently. First of all, some samples have been found to have very high microgel contents, up to 90% or greater. Secondly, during the analysis of these samples, invariably a thick, slimy layer will build up on the surface of the membrane and the flow rate will decrease drastically. Because of these unusual characteristics, it was felt that a more detailed study of the filtration characteristics of some of our high microgel polymers was warranted. An investigation into the extent to which solution concentration caused nonideal filtering conditions was made. Samples of smoked-sheet natural rubber (SSNR), emulsion polybutadiene (EmPBD), and acrylonitrile/butadiene rubber (NBR) containing microgel were studied using the experimental procedures published earlier.¹ Using a nonagitated filtration cell, an attempt was made to determine the conditions needed to achieve complete separation of microgel and soluble polymer, thus allowing for the

accurate determination of per cent microgel. A brief look at the effect ultrafiltration has upon the molecular weight distribution (MWD) was also made. After establishing guidelines for proper ultrafiltration using the nonagitated cell, an agitated cell filtration apparatus was evaluated for its ability to properly separate microgel from soluble polymer molecules, especially relative to the effectiveness of the nonagitated filtration cell.

EXPERIMENTAL

The 100-ml, 47-mm nonagitated filtration apparatus and the 500-ml, 900-mm agitated filtration apparatus were purchased from the Millipore Corp., Bedford, Mass. Membranes of 0.45-micron and 0.20-micron pore size were purchased from the Millipore Corp. and Gelman Co.

The experimental procedures used in the study of the nonagitated cell was exactly as described earlier.¹ Two variables were systematically altered: the solution concentration and the volume of solution that was filtered. Fifty milliliters of the original solution was poured into the filter barrel, and then a known volume was pressure filtered into a receiving vial. Microgel content was determined by evaporating an appropriate aliquot of the filtrate and comparing the dried weight per volume to the original concentration.

Filtration experiments with the agitated filtration cell were similar to those performed with the nonagitated cell, except that the volume poured into the filter barrel and the volume filtered were increased to as much as 500 ml.

GPC analyses were performed on a Waters Model 100 chromatograph operated on chloroform at 25°C. A flow rate of 1 cc/min and the differential refractometer detector were used. The columns were 4 foot \times $\frac{3}{8}$ in. styragel columns of the following porosities: 10^7 , 10^4 , 10^4 , and 10^2 Å.

DISCUSSION

A general theory of ultrafiltration has been proposed encompassing the concept of concentration polarization (CP).⁵⁻⁷ During ultrafiltration, accumulation of microgel (retentate) at or near the membrane surface restricts solvent flow and restricts the passage of soluble polymer (permeate) through the membrane. This microgel layer consolidates further, forming a secondary membrane of even greater restriction. This consolidation can be rapid. As an illustrative hypothetical example, consider a 0.2% solution of polymer that is 20% microgel. After filtering only 1 cc of this solution past a circular membrane of 47-mm diameter (the size of the nonagitated cell), a layer of microgel particles will build up on the membrane that is anywhere from about 200 particle diameters thick (assuming each microgel particle is 100 million molecular weight and the spherical diameter of these molecules is 0.45 micron) to as much as 20,000 particle layers thick (assuming a molecular weight of only 1 million). Thus, only a finite volume flow past the membrane is possible before the membrane becomes coated. Continuing to filter after coating is complete will cause the developed microgel layer to retain soluble polymer molecules that would normally have flowed through the uncoated filter membrane. In effect, then, this microgel layer is acting as a membrane of tighter porosity than the filter membrane itself. This flow behavior is largely

one of bulk flow transport (rather than diffusion of the microgel particles) to the surface of the membrane.^{8,9} Thus, agitating the solution immediately above the surface of the membrane can retard the buildup of this layer.^{2,3,5,6}

RESULTS

Nonagitated Ultrafiltration

The theory of ultrafiltration has never been thoroughly tested on synthetic polymers in conventional organic solvents. Since the manner in which some of our polymers filtered suggested that a mechanism similar to that just discussed was taking place, a study similar to that done by Baker³ was established to determine the filtration characteristics of high microgel polymers. Three rubber types were selected for study based on previous laboratory analyses showing that these families were among those containing the highest measured microgel contents. Benzene solutions of smoked-sheet natural ethyl rubber (SSNR) and emulsion polybutadiene (EmPBD) and methyl ketone solutions of acrylonitrile-butadiene rubber (NBR) of nominal 33% AN content were studied. Gel results using the standard macrogel/microgel procedure¹ are shown in Table I. All three contained appreciable microgel and were free of macrogel, making them excellent models for this study.

To evaluate the ultrafiltration of these samples and the occurrence of CP, repeated analyses of each rubber were made, systematically varying solution concentration and volume filtered. Figure 1 shows the results of microgel analyses obtained for the SSNR sample dissolved in benzene. Filtration was done using 0.45-micron filters. The apparent microgel content was plotted versus the volume filtered. Separate plots are shown for each of the concentrations 0.02%, 0.05%, 0.1%, 0.2%, and 0.5%. Owing to the low weight of rubber solids in the aliquots, it was impossible to obtain experimental data points below the concentrations and filter volumes shown in Figure 1. However, this did not present too great a problem in the interpretation of the data, as the plots could all be logically drawn as shown. Calculated apparent microgel results ranged from 88% to 24%. The data in Figure 1 showed two trends taking place. For each concentration, the apparent microgel content increased as the volume filtered was increased. Also, for any given filter volume, the apparent microgel increased as the concentration was increased. All the plots tended to converge at around 24%. It was observed that for all analyses yielding microgel contents higher than this limiting value (24%), a reduction of filter flow rate was encountered. Also, the membrane was found to be coated with a thick, slimy layer of microgel. However, when measurements resulted in microgel values close to 24%, the membranes were essen-

TABLE I
Gel Contents Using Standard Macrogel/Microgel Test

Rubber	Solvent	% Microgel	% Macrogel
Smoked-sheet natural rubber (SSNR)	benzene	73	0
Emulsion polybutadiene (EmPBD)	benzene	30	0
Acrylonitrile/butadiene (NBR)	MEK	74	0

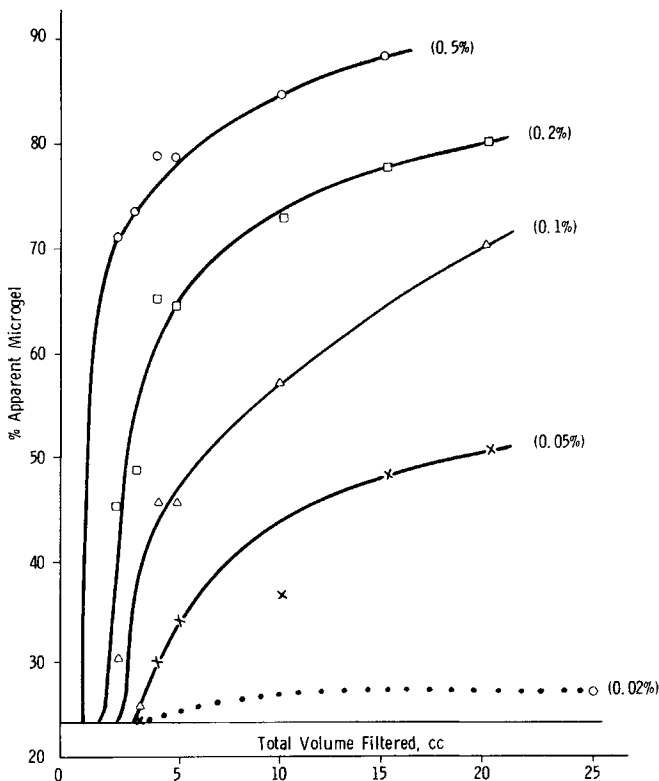


Fig. 1. Microgel content of smoked-sheet natural rubber.

tially clean, with little or no buildup of microgel and with no observable reduction in flow rate.

Although there is no way of knowing the actual microgel content of this sample of natural rubber or the other samples analyzed, it is presumed that this convergent value, arrived at by a double extrapolation to zero concentration and zero filter volume, corresponds to a value near the actual microgel content. This extrapolation approach has been used successfully by Baker³ to accurately measure standardized solutions of gel-like materials. In light of the fact that microgel is arbitrarily being defined here as that polymeric material that will not pass through a membrane of 0.45-micron pore diameter, this does not appear to be a limitation to the discussion presented here; that is, the extrapolated value can be assumed to be the correct microgel content.

The same general trends, with the same characteristic curve shapes assigned to each concentration isobar, were observed for EmPBD in benzene (Fig. 2) and NBR in MEK (Fig. 3) using the 0.45-micron filter. Limiting microgel contents for all samples are listed in Table II. In Figure 4, results of an analysis of the emulsion polybutadiene sample in benzene using 0.20-micron filters are shown. The limiting microgel content was greater than that measured using 0.45-micron filters, as expected due to the smaller pore size of the filter membrane.

The characteristic shapes of the individual curves in all these graphs appeared to be consistent with those predicted from the general theory of ultra-

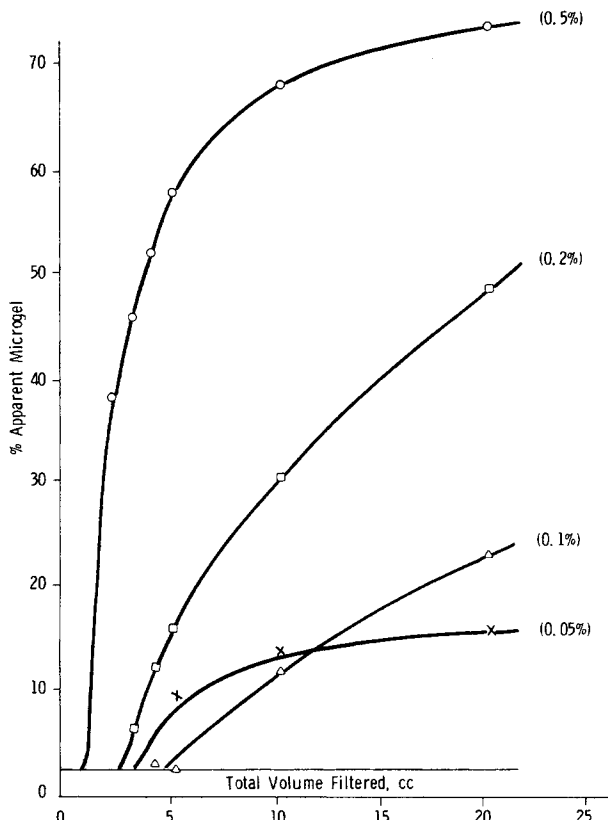


Fig. 2. Microgel content of emulsion polybutadiene rubber.

filtration. For any solution concentration, there is a finite volume that can be filtered while still maintaining ideal conditions, i.e., the apparent microgel content remained constant over this region. For example, for SSNR at 0.2%, only about 1 ml could be filtered before the apparent microgel value would begin to climb; whereas, at 0.02%, a higher volume could be filtered before the apparent microgel value would increase. To obtain ideal filtration, a choice must be made between filtering a large volume of a smaller concentration or a smaller volume of a larger concentration. This presents a real problem in the microgel test, since a gravimetric weighing of the solids in an aliquot of filtrate must be made. One milliliter of filtrate of a 0.2% solution of SSNR would contain only about 0.0014 g, whereas 25 cc of a 0.02% solution would

TABLE II
Microgel Results Using Extrapolation Procedure

Rubber	Solvent	% Microgel
SSNR	Benzene	24
EmPBD	Benzene	3 ^a
NBR	MEK	6

^a 18% Using 0.20-micron filter membranes.

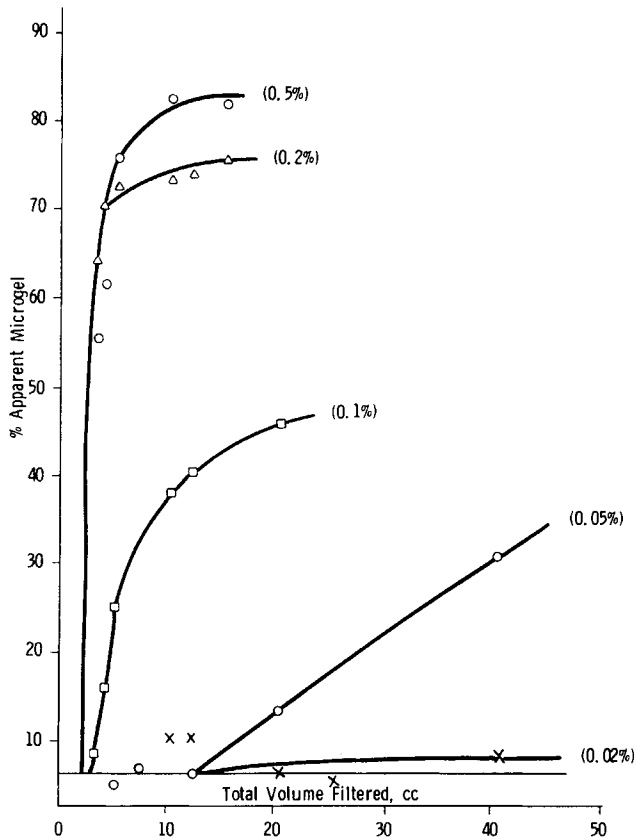


Fig. 3. Microgel content of acrylonitrile/butadiene rubber.

contain around 0.0035 g (assuming 30% microgel content). These are small weights, almost the limit of measurement using the balances in our laboratories, and large errors can be introduced during the weighing step. Also, the microgel test contains a multiplication factor dependent on the aliquot taken. For example, if a 1-ml aliquot is used, the weight (and the error in the weight) is multiplied by 100; whereas, if a 25-ml aliquot is taken, the weight (and the error in the weight) is multiplied by only 4. Thus, to minimize errors, larger weights are needed and larger volumes must be filtered.

Gel Permeation Chromatography

The manner in which the apparent microgel varies, as shown in Figures 1-4, could also result in changes in the molecular weight distribution (MWD) of the polymer that flows past the membrane. This was investigated using the emulsion polybutadiene (EmPBD) sample and a Waters Model 100 GPC operated on chloroform. From Figure 2, it was observed that at 0.1% benzene solution, CP, i.e., the onset of nonideal ultrafiltration, occurred at around the 5-cc filter volume region. Using this as a guide, separate 0.1% chloroform solutions were filtered to the various total filter volumes shown in Figure 5, encompassing the range 1 to 25 cc. Each filtrate was analyzed using

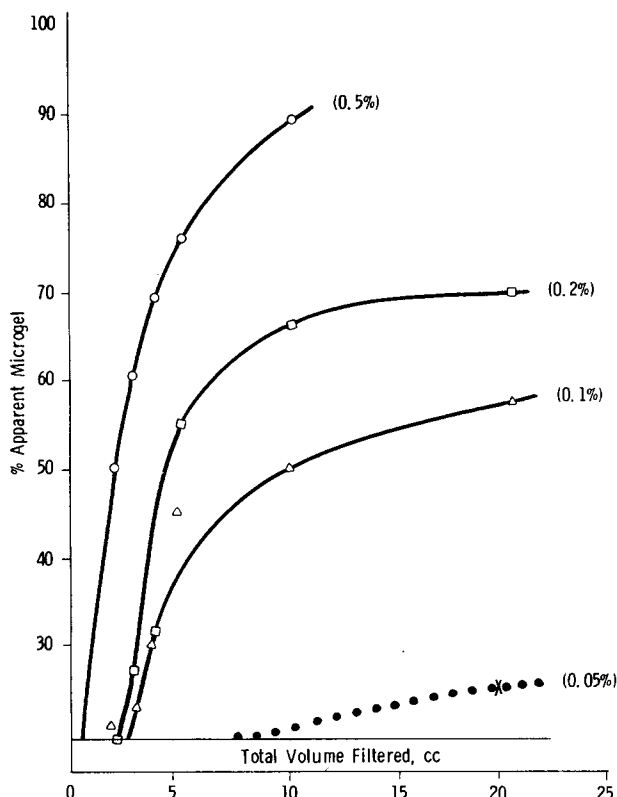


Fig. 4. Microgel content of emulsion polybutadiene rubber (0.2-micron membrane).

GPC to obtain MWD data. The normalized GPC curves shown in Figure 5 revealed that the MWD remained essentially constant over the filter volume range 1 to 5 cc, but then a decrease in the high molecular weight region appeared at 10 cc filter volume. The high molecular weight components decreased even further through 25 cc filter volume. In Figure 6, the area under the GPC chromatogram (which is proportional to polymer concentration) was plotted versus the filter volume. It was apparent that the polymer concentration remained constant up to around 5 cc filter volume, then began to gradually decrease, in agreement with the apparent microgel data.

Filtration Guidelines

These results illustrate that it is important to carry out the ultrafiltration step under ideal filtering conditions when either the microgel content is being measured or MWD data are being obtained via GPC. Ideally, to accurately determine microgel content for a sample, a complete extrapolation plot similar to those shown in Figures 1-4 should be made. Since this is a practical impossibility, an alternate approach must be taken. Probably, a more viable means would be to adjust the concentration from sample to sample so as to maintain rapid flow rate with low applied pressure, since it has been observed that on-set of nonideal filtering was found to coincide with a reduction in filtering rate.

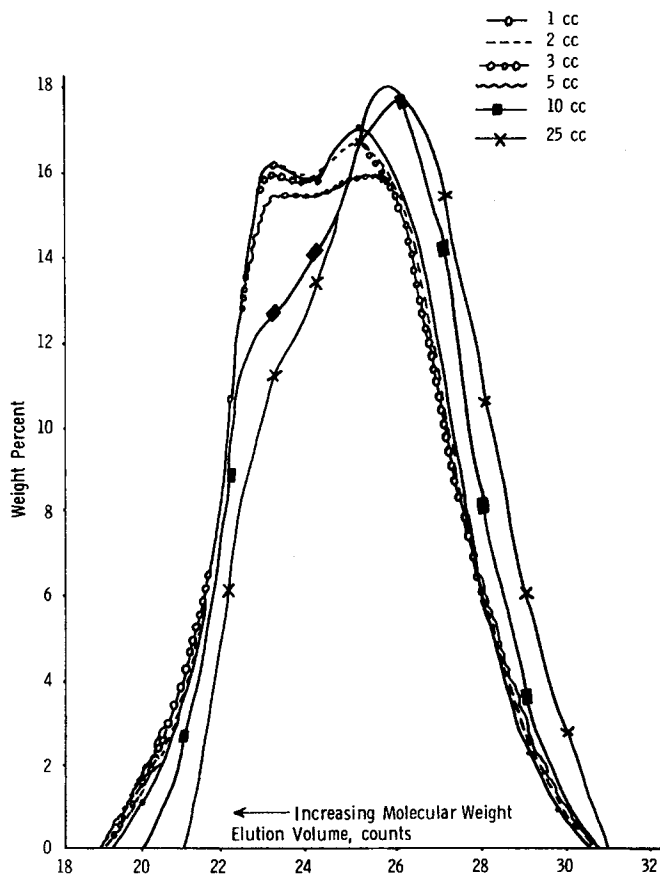


Fig. 5. Molecular weight distribution changes in emulsion polybutadiene.

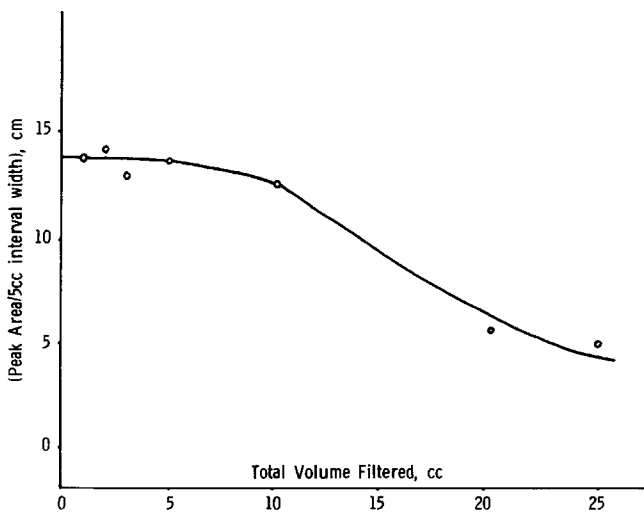


Fig. 6. Emulsion polybutadiene: change in concentration with filter volume determined by GPC.

Agitated Ultrafiltration

All the data discussed previously were obtained using the standard 100-cc, 47-mm nonagitated filter cell. The results revealed that with this cell, only very small volumes of samples (1 cc or less) could be properly filtered when using concentrations of 0.2% or more. These small volumes inhibit the use of filtration as part of other testing, for examples, quantitative microgel or GPC analyses (GPC analyses require a minimum of 3 cc for injection into the chromatograph). Consequently, a way had to be found to increase the allowable volume filtered while still maintaining ideal filtration. It has been shown by others^{2,3,5,6} that nonideal filtration of other polymeric systems can be reduced using an agitated cell. Therefore, an agitated 500-cc, 90-mm filtration apparatus was evaluated as a possible means of obtaining these desired conditions.

An extensive analysis of the agitated filtration cell as was done for the nonagitated cell was not made here as it has already been shown by several authors^{2,3,5,6} that the use of agitation does not alter the characteristics of CP but only retards its occurrence. The experiments discussed here were intended simply to observe if in our systems an increase in filtering efficiency could be obtained. A second sample of SSNR (different from that used in the studies of the nonagitated cell) was used. This sample, when analyzed with the nonagitated cell so that CP was not observed, was found to contain 23% microgel. When analyzed using the standard macrogel/microgel test,¹ 59% microgel was calculated.

As an initial experiment with the agitated ultrafiltration cell, two separate 500-cc volumes of a 0.25% benzene solution of SSNR were filtered, one solution being agitated during filtration, the other solution not agitated during filtration. Table III summarizes the results.

In both cases, filtration progressed from ideal to nonideal, since the filtration rate decreased before the entire 500 cc had been filtered. However, the fact that the total time needed to filter 500 cc decreased because of agitation, and the fact that a lower microgel value was determined with agitation, indicated that CP had been retarded by agitation. However, since both microgel values were higher than 23%, this indicated that agitation did not prevent CP from occurring but only retarded it.

The experiment was repeated and altered in an effort to eliminate CP completely, i.e., obtain a value close to 23% microgel at 0.25% concentration. This time, only 10 cc was filtered under agitation. The filtration rate was extremely rapid and showed no signs of decreasing. In addition, the 10-cc aliquot provided suitable precision in both the volumetric and gravimetric steps in the microgel analysis. Microgel content was calculated as 16%. The cause of the lower value (16% versus 23%) was not investigated further; rather, it was assumed that the earlier analysis, in which 23% microgel was calculated,

TABLE III
Filtration of 0.25% SSNR Benzene Solutions

Solution agitated	Volume filtered, cc	Time needed, min	% Microgel
Yes	500	15	46
No	500	60	68

was done under the influence of some degree of CP. However, the fact that 16% microgel was obtained here did suggest that, for this sample, at least 10 cc of a 0.25% solution could be filtered properly using agitation, whereas before only 1 cc could be properly filtered when agitation was not used. Thus, the agitated cell did improve the filtering characteristics of high microgel solutions beyond that of the nonagitated filtration cell. With this improvement, larger volumes and higher concentrations of polymer solutions can be processed in reasonable amounts of time, providing suitable material for other evaluations, whether it be GPC analyses or quantitative microgel analyses.

CONCLUSIONS

Studies using the standard 100-cc, 47-mm nonagitated filtration cell revealed several trends:

1. At constant polymer concentration, the measured microgel content of the polymer increased as the total volume filtered was increased. Higher concentrations gave higher microgel contents at a constant filter volume.
2. For any given solution concentration, there was found to be a limit to the volume of solution that could be filtered and still achieve separation of microgel and soluble polymer. This limit increased as the solution concentration decreased. When this limit was exceeded, soluble polymer was retained by the microgel.
3. The soluble polymer in the initial increments of filtrate collected had the same molecular weight, but at higher filter volumes, the molecular weight continually decreased as the filtrate volume was increased.

All these observations are explainable by characteristics of concentration polarization. Being able to maintain the initial flow rate with minimal applied pressure was usually sufficient evidence to denote when proper separation of microgel and soluble polymer was occurring. Cessation of these conditions marked the beginning of incomplete separation of the microgel and soluble polymer.

The use of an agitated 500-cc, 90-mm filtration cell retarded the occurrence of CP beyond that of the nonagitated cell and allowed larger volumes and higher concentrations of polymer solutions to be properly filtered.

Ultrafiltration can be an adequate technique for the measurement of microgel, however, for accurate determinations to be made, alterations to the original published test procedure¹ must be made in light of what has been shown here. In particular, an agitated filtration cell may have to be employed.

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References

1. J. R. Purdon and R. D. Mate, *J. Polym. Sci. A1*, **8**, 1306 (1970).
2. J. E. Flimm, Ed., *Membrane Science and Technology*, Plenum Press, NY, 1970.
3. R. W. Baker and H. Strathmann, *J. Appl. Polym. Sci.*, **14**, 1197 (1970).

4. F. Bellucci, E. Drioli, and V. Scardi, *J. Appl. Polym. Sci.*, **19**, 1639 (1975).
5. M. C. Porter and A. S. Michaels, *Chem. Technol.*, 56 (Jan. 1971).
6. W. F. Blatt, *Amer. Lab.*, 78 (Oct. 1972).
7. C. M. Good, A. R. Reti, and M. S. Krongelb, *Amer. Lab.*, 71 (Oct. 1974).
8. H. Yasuda and A. Peterlin, *J. Appl. Polym. Sci.*, **17**, 433 (1973).
9. M. R. Ambler, unpublished results.

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