

# The Effect of Plasticization and pH on Film Formation of Acrylic Latexes

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## SYNOPSIS

The effect of several variables relevant to film formation in 49 : 49 : 2 poly(methyl methacrylate-*co*-butyl acrylate-*co*-methacrylic acid) latexes were studied.

Plasticization of the terpolymer by both an anionic [sodium dodecyl benzene sulphonate (NaDBS)] and a nonionic [nonyl phenol ethylene oxide adduct (NP40), forty ethylene oxide units on average] surfactant were investigated. Dynamic mechanical measurements indicated that NP40 plasticized the polymer, whereas NaDBS did not. This was attributed to the compatibility of the nonionic emulsifier and the polymer. The influence of the surfactants on the film formation process was studied using minimum film temperature (MFT) measurements and scanning electron microscopy (SEM). As expected, the MFT was independent of NaDBS concentration. However, the MFT was also independent of NP40 concentration. Film formation was further investigated using SEM. The series of micrographs at varying NaDBS concentrations showed no effect on the degree of film fusion. However, surface exudates were observed. The micrographs revealed that increasing NP40 content resulted in an apparently greater degree of film coalescence. That is, there was bridging of the particles in the interstitial regions. This was attributed to localized plasticization of the polymer in these regions by NP40.

The effect of water plasticization of the latex polymer was studied using dynamic mechanical measurements. The physical character of the terpolymer was varied using mol wt modifiers (CBr<sub>4</sub> chain transfer agent and ethylene glycol dimethacrylate crosslinker). It was found that all of the polymers were plasticized by water.

Finally, the film forming behavior was investigated as a function of latex pH. MFT measurements indicated an independence of pH. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Water based coatings are comprised of a wide array of ingredients, many of which may influence the performance of the coating. Similarly, the emulsion polymer binder is produced from a number of reactants. Thus, the film forming behavior, along with other characteristics of a latex is not governed by the properties of the constituent polymer alone. Several ingredients, integral to the emulsion polymer synthesis, may influence properties of the latex and the resulting commercial coating. Two of these latex

components, which are used in most research and all commercial systems, are emulsifier and water.

Two types of emulsifiers are commonly selected to stabilize emulsion polymerization reactions. In addition to preventing coagulation during polymerization, the emulsifiers impart long-term colloidal stability to the latex. Anionic surfactants provide stabilization via electrostatic repulsion of the ionic groups on neighboring latex particles. The bulky character of nonionic surfactant molecules impart stabilization sterically. In commercial systems, either or both types of surfactant are added during the reaction and subsequent to polymerization in order to enhance stability.

Much of the early research into the role of surfactants during latex film formation was conducted

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by Bradford and Vanderhoff. The effect of the post-addition of nonyl phenol ethylene oxide adducts of varying ethylene oxide chain length to poly(styrene-*co*-butadiene) latex was investigated.<sup>1</sup> The polyoxyethylene chain length ranged from four (NP4) to forty (NP40), resulting in a range of physical properties. The smaller molecules were soluble in oil, whereas the larger molecules had a limited solubility in oil, but were soluble in water. Of the series of emulsifiers examined, only NP20 and NP40 exuded from the latex films upon aging. However, over time, the exudates completely disappeared. This phenomenon was attributed to the oxidation of the surfactant molecules at the polymer/air interface, yielding smaller molecules that were compatible with the polymer.

Bradford and Vanderhoff studied the effect of plasticizers on nonfilm-forming latexes.<sup>2</sup> They found that the postaddition of a number of plasticizers would promote film coalescence. However, this effect was not discernible immediately. Apparently, fusion occurred only upon aging of the films. It was postulated that the rate of coalescence was limited by the rate of diffusion of the water soluble plasticizer into the polymer particles.

In another work, Bradford and Vanderhoff<sup>3</sup> found that a 67 : 33 ethyl acrylate/methyl methacrylate copolymer underwent further gradual coalescence. This was not, however, accompanied by surfactant exudation. It was not explicitly stated that a nonyl phenol ethylene oxide adduct emulsifier was used, but that is assumed to be the case.

Bradford and Vanderhoff<sup>1</sup> also studied the exudation of inorganic salts resulting from the ionic initiators used in the emulsion polymerization. Exudations of about 0.05  $\mu\text{m}$  in size were noticed on the film surface. These exudates were virtually eliminated when the latexes were dialyzed and ion exchanged prior to casting of films.

Padget and Moreland<sup>4</sup> found that block copolymer surfactants, such as ethylene oxide/propylene oxide/ethylene oxide, plasticized chlorine-containing vinyl acrylic latex copolymers. They found that the film coalescence process was accelerated by the presence of these materials, as revealed by electron microscopy. The rate of fusion increased with increasing stabilizer content up to the concentration at which the polymer particle surfaces became saturated with surfactant molecules. No effect on the minimum film formation temperature of the latexes was observed.

Interactions between the polymer latex and surfactants are important when considering the plasticization phenomenon. Edelhauser<sup>5</sup> found that an-

ionic surfactants [sodium lauryl sulphate (NaLS) and sodium dodecyl benzene sulphonate (NaDBS)] can penetrate into polyvinyl acetate latex particles. The emulsifier penetration is accompanied by water imbibition, causing swelling and the eventual dissolution of the polymer particles. This effect depends on the mol wt of the surfactant molecule.<sup>6,7</sup> In the case of NaLS, this effect is lessened when the vinyl acetate is copolymerized with butyl acrylate, and does not occur for polystyrene and poly(methyl methacrylate-*co*-ethyl acrylate) latexes.<sup>6</sup>

The influence of emulsifiers on the minimum film forming temperature (MFT) of VAc/BA latexes was investigated by Vijayendran et al.<sup>6</sup> They found that an hydrophilic nonionic surfactant (i.e., high HLB value) has a more pronounced effect on lowering the MFT than a less hydrophilic surfactant, in a homologous pair of nonyl phenol ethylene oxide adducts. That is, the surfactant possessing more ethylene oxide units has a more pronounced effect, due to the compatibility of the hydrophilic emulsifier and the slightly hydrophilic copolymer. The authors also present electron micrographs that reveal a higher degree of coalescence for films containing the high HLB surfactant than for films free from emulsifier.

In the case of anionic NaLS in a VAc/BA copolymer latex, exudation appears to occur.<sup>6</sup> This is attributed to the solubilization of the polymer by the surfactant, as discussed above. The authors suggest that the hydrophilic solubilized material may be exuded to the film surface due to its incompatibility with the less hydrophilic base polymer.

In other work related to the adsorption of NaDBS on PMMA and PS latexes, Paxton<sup>8</sup> found that the emulsifier was less likely to adsorb on the more polar of the two surfaces.

The present research was undertaken to determine whether common anionic and nonionic surfactants have a plasticizing effect on a poly(methyl methacrylate-*co*-butyl acrylate) binder polymer. Two emulsifiers, typically used in latex syntheses, were chosen for study. The anionic surfactant selected was sodium dodecyl benzene sulphonate (NaDBS). The nonionic surfactant chosen was a nonylphenol ethylene oxide adduct, containing 40 ethylene oxide units on average (NP40). Both of these emulsifiers are frequently employed in industrial processes, and are representative of the two surfactant types. Dynamic mechanical measurements were made with surfactant-free polymer and the same material containing either the anionic or the nonionic emulsifier. The minimum film temperature was measured as a function of the concen-

tration of both surfactants. Finally, scanning electron microscopy was utilized to examine the dried films cast from latexes containing varying amounts of both stabilizers.

Another characteristic of a latex that may affect film formation is the pH. Often, emulsion polymerizations are initiated by persulphate salts, resulting in a low pH product emulsion. In commercial applications, the acidity is generally adjusted by ammonium hydroxide addition in order to yield a pH of approximately 9. In an early work on latex film performance, Cogan<sup>9</sup> found that the minimum film temperature of a homopolymer vinyl acetate latex increased dramatically when the pH was raised. It was also observed that the addition of soluble salts to the latex formulation increased the minimum film temperature. The present work includes an investigation in order to determine if similar behavior occurred with poly (butyl acrylate-*co*-methyl methacrylate).

Evidently, water is an indispensable ingredient in emulsion polymerizations. It is conceivable that water could have a plasticizing effect on film forming copolymers, particularly those possessing some hydrophilic character. Since water is present in varying concentrations throughout the film formation process, it is important to determine the influence of water on the film fusion process. Dynamic mechanical measurements were employed here to investigate the water plasticization of a series of poly (butyl acrylate-*co*-methyl methacrylate) latexes having varying degrees of crosslinking.

It is necessary to ascertain if polymer plasticization occurs (whether via water imbibition or surfactant addition) since the accompanying viscosity and modulus reductions should directly affect the degree of film fusion. Several models of the second stage of film formation have been proposed, which relate the film forming behavior to the polymer modulus.<sup>10-14</sup> Other theoretical approaches have suggested that a relationship exists between the polymer viscosity and film coalescence.<sup>12-15</sup> In previous research conducted in this laboratory,<sup>16</sup> a model of film formation was proposed that related the degree of particle fusion to both the inverse modulus and the inverse viscosity.

These theoretical models of film formation indicate that the modulus and viscosity reduction resulting from plasticization should promote film coalescence. However, an opposing effect is expected in the case of surfactant-plasticized material, due to the influence of emulsifier on the surface energetics of the system. It has been suggested that the surface tension of water, present in the channels between

the latex particles,<sup>10,11,13,14,16</sup> the polymer surface tension,<sup>15,17</sup> and the polymer/water interfacial tension<sup>11,14,16,17</sup> are possible driving forces for film fusion. An increase in the surfactant concentration will produce a decrease in the magnitude of these parameters, thus, in theory, inhibiting film coalescence. Thus, the influence of water in the coalescence process is not clear without experimentation.

## EXPERIMENTAL

### Emulsion Polymerization

Latexes were synthesized using a semicontinuous reaction scheme. The proportions of all reactants, except for the mol wt modifiers, were kept constant between the various recipes. The basic emulsion polymerization recipe is given below. Table I provides information about the mol wt modifiers used, and the resulting particle size and particle size distributions.

#### Basic Emulsion Polymerization

Reactor Charge:	
Deionized water	210 g
Ammonium persulphate initiator	1.35 g
Monomer mixture	
Butyl acrylate	101.4 g
Methyl methacrylate	101.4 g
Methacrylic acid	2.55 g
Mol wt modifier	<i>x</i> g

All reactions were carried out in a 1 L kettle reactor, equipped with an overhead condenser and a jacketed mechanical stirrer. The stirring rate was maintained at 250 rpm throughout the reaction.

The water and initiator were charged to the reactor and were maintained at a temperature of 80°C with continuous stirring. The monomer mixture was

**Table I Emulsion Polymer Mol Wt Modifiers and Particle Size Distributions**

Latex	Modifier	<i>x</i> (g)	$D_n$ (nm)	$D_w/D_n$
L1	CBr <sub>4</sub>	2.50	680	1.03
L2	CBr <sub>4</sub>	0.96	606	1.01
L3	—	—	580	1.01
L4	EGDM <sup>a</sup>	8.00	899	1.007
L5	EGDM <sup>a</sup>	12.00	984	1.006

<sup>a</sup> Ethylene glycol dimethacrylate.

fed to the reactor via a fluid metering pump at a constant rate of approximately 1 mL/min. No monomer accumulation was observed at any time. Therefore, it was assumed that the reaction was starve-fed and that the composition of the terpolymer was uniform throughout the latex particle. When monomer addition was complete, the reaction was continued for 1 h. The latex was then gradually cooled to ambient temperature. Finally, the latex was filtered through an 100-mesh screen to remove the minimal amount of grit formed during the polymerization.

Latex particle size measurements were obtained using an ICI-Joyce Loeb Disk Centrifuge, according to a method described elsewhere.<sup>19</sup>

## Dynamic Mechanical Measurements

### Sample Preparation—Surfactant Plasticization

Latex polymerized without the addition of the mol wt modifiers was chosen for these experiments. Both the nonionic and anionic surfactants were added to the latex subsequent to reaction to yield a final concentration of 0.041 g emulsifier/g polymer, which is a typical value for a commercial product. Samples were then prepared for testing in the manner described below.

### Sample Preparation—Water Plasticization

It was desired to perform all dynamic mechanical tests on completely fused polymer samples, since it was thought that the film integrity might effect the response of the material. The latexes were dried in a convection oven at 60°C and then were ground in a Wiley mill. All samples were then thoroughly fused by pressing at elevated temperature and pressure. The actual pressing conditions were varied since the materials have very different viscoelastic properties. Typical conditions were  $T = 100^\circ\text{C}$ ,  $P = 16$  psi for 60 s (polymer L1), and  $T = 100^\circ\text{C}$ ,  $P = 570$  psi for 900 s (polymer L5). All samples were pressed several times to ensure complete fusion.

The fused polymer sheets obtained were approximately 2 mm thick. Circular samples of about 25 mm in diameter were cut from the sheets and were immersed in deionized water at room temperature. The specimens were exposed to water for 2 months.

### Dynamic Mechanical Temperature Sweeps

Measurements of the polymer moduli were made using a Rheometrics Model 605 mechanical spec-

trometer. Both torsion rectangular and parallel plate geometries were employed. In the case of the parallel plate geometry, 8 ( $10^{-3}$ ) m diameter and 25 ( $10^{-3}$ ) m diameter plates were used.

The initial strain experienced by the sample was chosen by preliminary experiments. Strain sweeps were performed at the lowest temperature in the experimental range and the highest frequency of those selected. Strain sweeps were performed to determine an initial strain value that fulfilled several criteria. Most important, the torque on the transducer had to be within the "safe" operating limits of the machine (this sets an upper limit for the strain). Also, the measurement of tan delta had to be within the measuring capabilities of the Rheometrics (this sets a lower limit for the strain). Finally, to allow comparison of the materials at different deformations and different geometries, it was necessary that the polymer behave in a linear viscoelastic manner at the strain chosen. Figure 1 is a typical strain sweep, which illustrates the linear viscoelastic nature of the materials tested.

For all experiments, forced oscillation measurements were obtained at three frequencies for each temperature in the temperature sweep experiments. At the lower end of the selected temperature range, torsion rectangular geometry was used because of the stiffness of the polymers. When the torque became unacceptably low, the torsion rectangular geometry was exchanged for the small parallel plate geometry. At the higher temperatures, the larger parallel plates were required. For all geometries, as the signal diminished with increasing sample temperature, the percent strain experienced by the specimen was increased. This procedure is only acceptably used in the linear viscoelastic strain region, where the dynamic mechanical response of the material is not a function of the degree of deformation. Linear viscoelasticity was confirmed by performing a strain sweep at the terminal experimental temperature for each geometry. As for the low temperature strain sweep, the test was done at the highest frequency used in the temperature sweep.

### Scanning Electron Microscopy (SEM) and Minimum Film Temperature (MFT)

An apparatus similar to that used by Protzman and Brown,<sup>20</sup> and ASTM method D2354, was used to determine the MFTs of the various latexes.<sup>21</sup> An insulated stainless steel bar replaced the aluminum bar in the original apparatus. Cooling at one end of the bar was achieved by two 12-V ceramic thermoelectric cooling modules. The cooling rate was

## L1 Strain Sweep Temperature=22°C

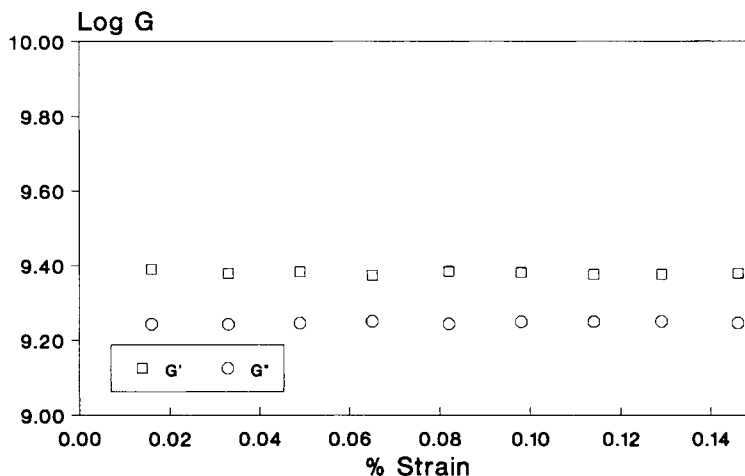


Figure 1

maintained by means of a feedback control device. Heat was not supplied at the opposite end of the bar, since all the MFTs were below room temperature. The temperature gradient along the bar was determined by eight thermocouples, installed at intervals along the bar. The thermocouples were connected to a digital temperature indicator, which had an accuracy of  $\pm 0.1^\circ\text{C}$ .

A glass plate, which permitted visual observation of the drying films, covered the stainless steel bar. Prior to application of the latexes, the cooling mechanism was activated and nitrogen gas flow from the cold to hot end of the bar at a rate of  $3.3 (10^{-5}) \text{ m}^3 \times \text{s}^{-1}$  was started. The  $\text{N}_2$  gas minimized the condensation of water at the cold end of the bar, and maintained the humidity at a constant level. The temperature of the bar was allowed to equilibrate for about 6 h. The glass plate was removed, approximately equal volumes of the latexes were applied to the channels down the length of the bar, and the glass plate was quickly replaced. Drying of the latexes took approximately 4 h. During this time, five replicate measurements of the temperature gradient along the bar were obtained and subsequently averaged. The MFT was determined as the temperature at which the clarity of the dried film was observed.

In order to ascertain the effect of emulsifier concentration on film formation, various concentrations of both NaDBS and NP40 were added postreaction to latex L3 (see Table I), and the MFTs were measured. For the measurement of MFT as a function of pH, ammonium hydroxide solution was added to

a series of 20 mL samples of latex L3. Since the pH drifts over time, replicate measurements at a particular pH could not be obtained. Hence, the pH of the latex was measured immediately prior to application on the MFT bar.

The coalescent behavior of the dried latex cast films was examined by scanning electron microscopy (SEM). Prior to exposure to the electron beam, the films were gold sputtered to a thickness of  $1.6 (10^{-4}) \text{ m}$  to prevent charging and deformation of the film surface.

## RESULTS AND DISCUSSION

### Surfactant Plasticization

The dynamic mechanical behavior of latex L3, both with and without postreaction emulsifier addition, is shown in Figures 2 and 3. All dynamic mechanical measurements were performed at three oscillation frequencies, but a single frequency ( $1 \text{ rad} \times \text{s}^{-1}$ ) only is shown for clarity. Figure 2 shows the dynamic mechanical behavior as a function of temperature for a NaDBS concentration of 0.041 g NaDBS/g polymer. Figure 3 shows the analogous information for NP40 at the same concentration.

Addition of the anionic (NaDBS) surfactant to a surfactant-free latex has no effect on the modulus. However, plasticization of the polymer is observed in the case of the nonionic surfactant. NP40 reduces the  $\log G^*$  approximately one half decade in the temperature range where film formation occurs

## L3 Dynamic Mechanical

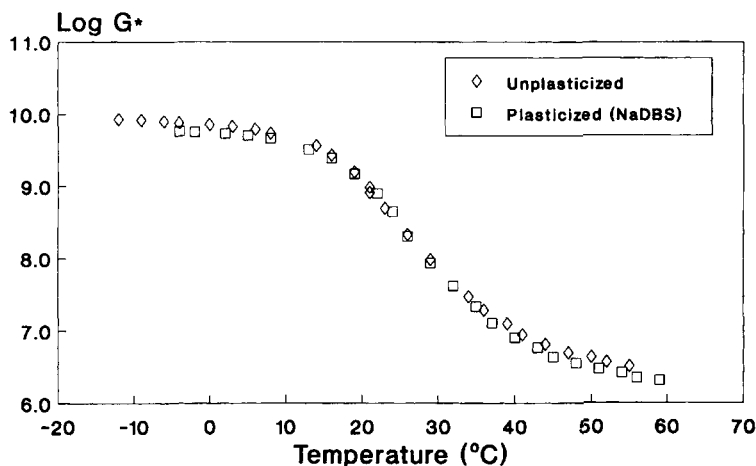


Figure 2

( $\sim 10^\circ\text{C}$ ). It should be noted that this difference is significant, since the data are of excellent quality and are highly reproducible. This is evidenced by the use of two geometries (torsion rectangular and parallel plate) to obtain these data. There are no discontinuities in the curves when the geometry is changed, which is indicative of linear viscoelastic behavior. This is a highly desirable operational mode for dynamic mechanical measurements.

A reduction in the polymer modulus should theoretically promote film fusion, since it results in a more deformable and less viscous material (i.e., the degree of film fusion is a function of  $1/G$  and  $1/\eta$ ). This effect should be countered by the effect of sur-

factant addition on the surface energetics of the system (i.e., the degree of film coalescence is a function of water surface tension,  $\sigma$ , and polymer/water interfacial tension,  $\gamma$ ).<sup>16</sup> At concentrations of surfactant below the critical micelle concentration (CMC) of the latex, changes in surfactant concentration should affect the surface energetics of the system. In the case of the particular latex studied, the CMCs are approximately 0.001 g NaDBS/g polymer and 0.008 g NP40/g polymer. At concentrations of emulsifier higher than the CMC, which corresponds to total particle coverage, additional surfactant should not affect the surface energetics nor the degree of film fusion, unless the polymer is plasticized.

## L3 Dynamic Mechanical

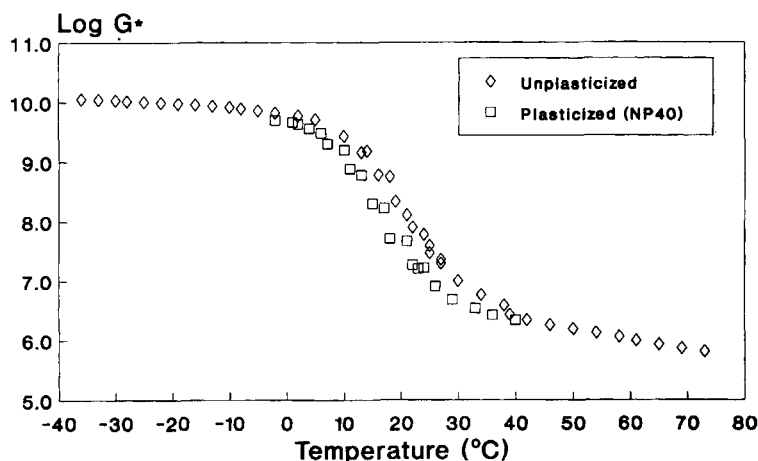


Figure 3

### MFT as a Function of NaDBS Surfactant Concentration

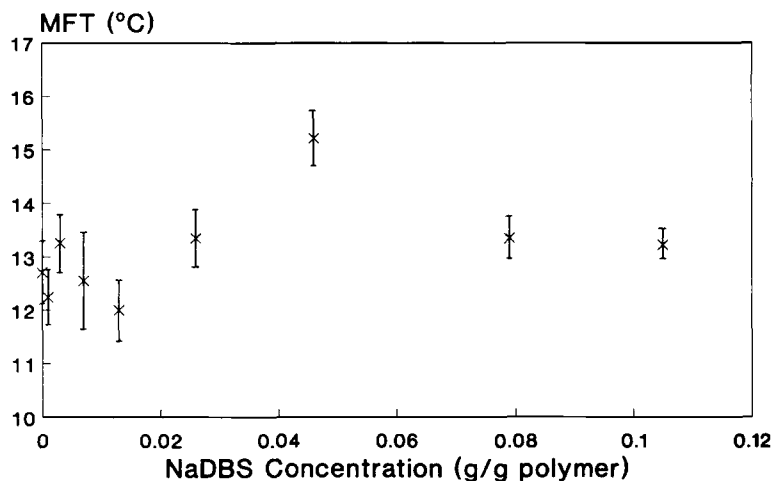


Figure 4

When polymer plasticization occurs, there should be an accompanying reduction in the minimum film temperature (MFT). Figures 4 and 5 show the MFT as a function of surfactant concentration for NaDBS and NP40, respectively. The error bars correspond to the standard deviations. Each data point shown corresponds to the average of replicate (usually four) measurements. As expected, the MFT of the latex containing excess NaDBS is not affected by surfactant concentration. Surprisingly, the same behavior

is observed for the latex containing postpolymerization-added NP40.

It was predicted that polymer plasticization would result in the lowering of MFT for the latex containing nonionic emulsifier. In order to investigate further the role of surfactant, SEM was employed to examine the fusion behavior of films dried with varying levels of surfactant. Figure 6 shows electron micrographs of dried films containing NaDBS. As predicted from the dynamic mechanical and mini-

### MFT as a Function of NP40 Surfactant Concentration

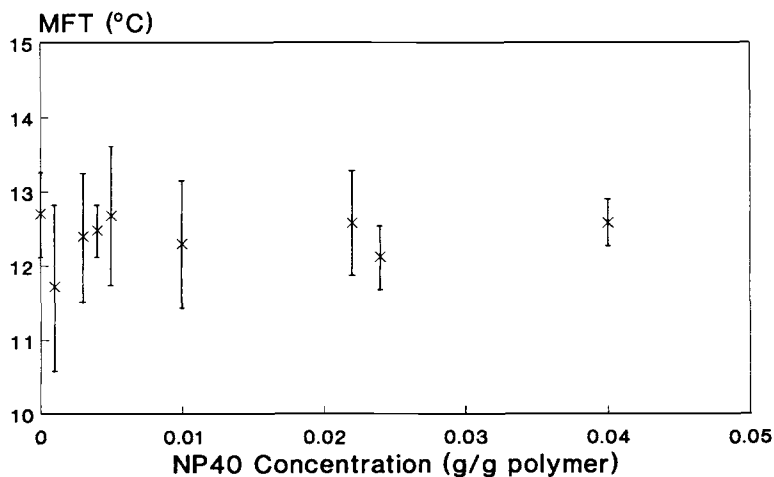
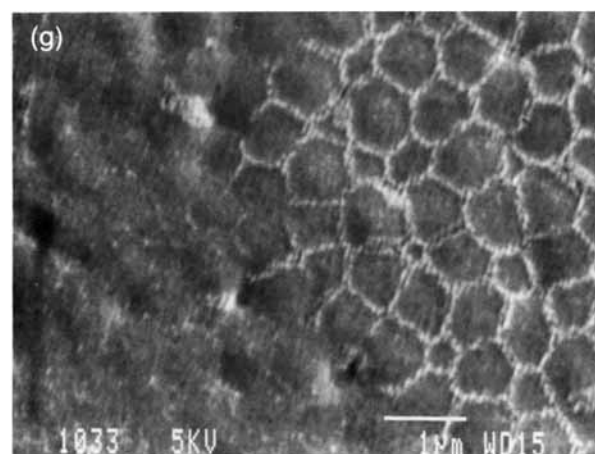
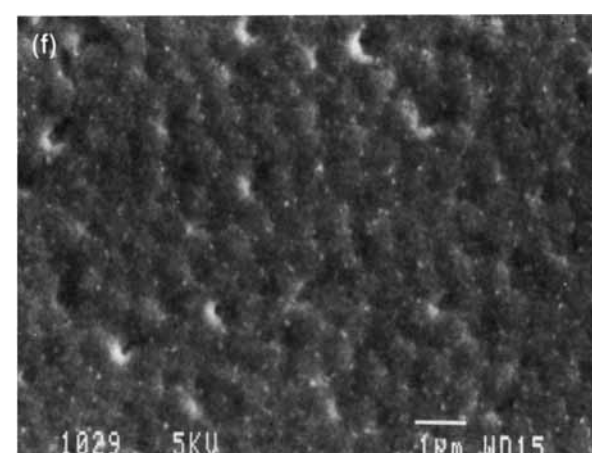
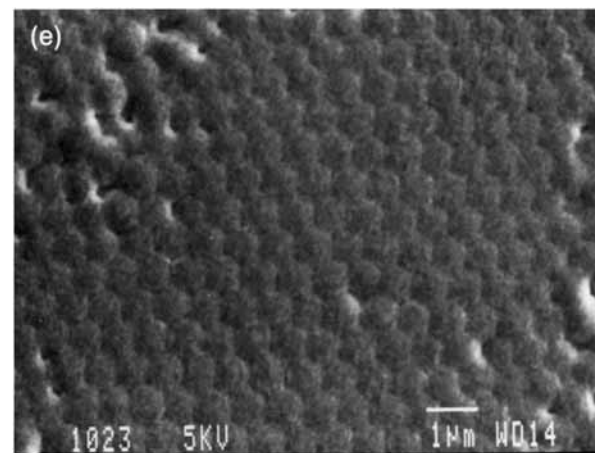
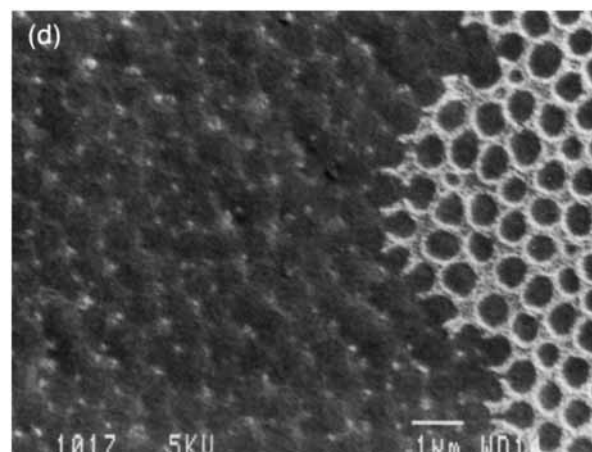
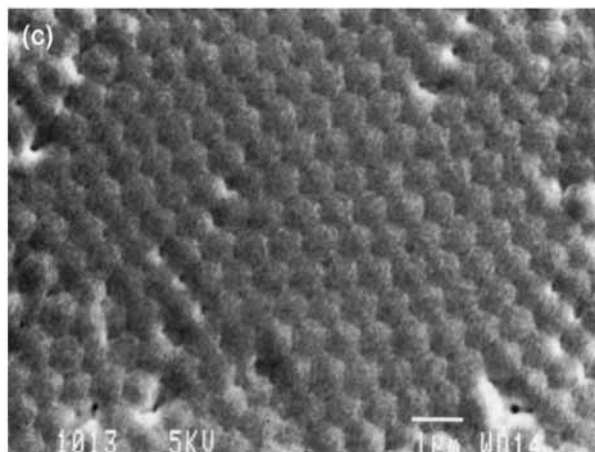
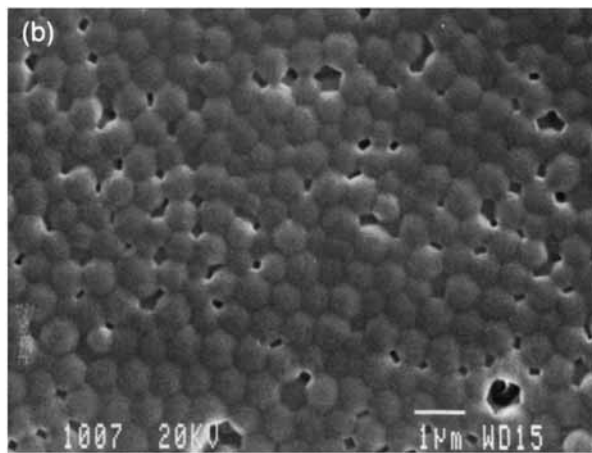
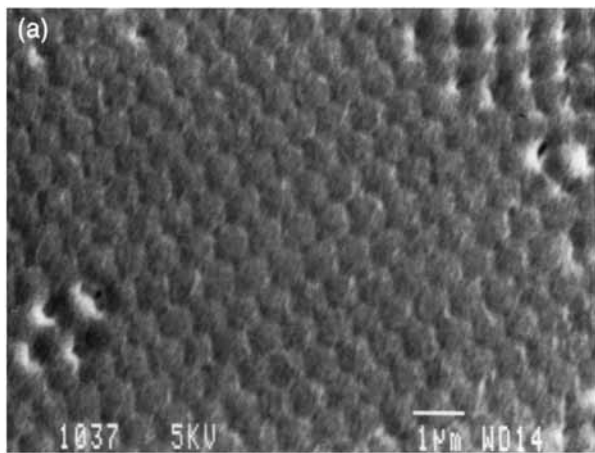


Figure 5



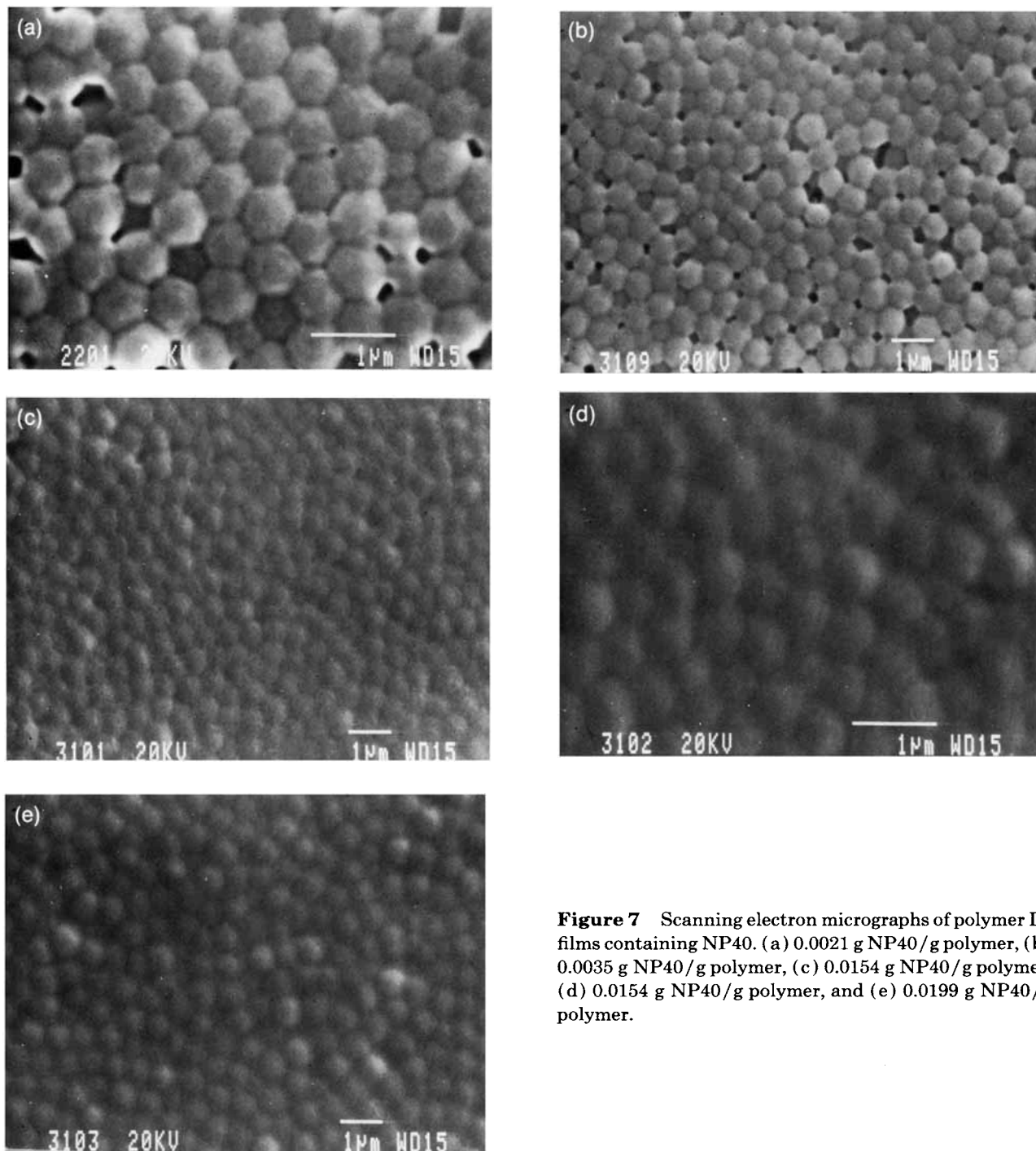
**Figure 6** Scanning electron micrographs of polymer L3 films containing NaDBS. (a) Surfactant free, (b) 0.0046 g NaDBS/g polymer, (c) 0.0090 g NaDBS/g polymer, (d) 0.0107 g NaDBS/g polymer, (e) 0.0155 g NaDBS/g polymer, (f) 0.0194 g NaDBS/g polymer, and (g) 0.0206 g NaDBS/g polymer.



mum film temperature results, there is no discernible increase in the degree of fusion as the NaDBS concentration is increased. However, regions of unusual morphology were revealed. This phenomenon is not unique to the films containing NaDBS, but is also observed with surfactant-free latexes. The phenomenon is likely due to the exudation of either pseudosurfactant, generated during the emulsion polymerization,<sup>18</sup> or the exudation of inorganic salts.<sup>1</sup>

Pseudosurfactant molecules are oligomeric or polymeric chains with terminal sulphate groups, resulting from initiation of polymerization via thermal decomposition of persulphate initiator.

The scanning electron micrographs of films containing excess NP40 are shown in Figure 7. As the concentration of the nonionic surfactant is increased, the degree of film coalescence appears to increase. As discussed earlier, there are two com-



**Figure 7** Scanning electron micrographs of polymer L3 films containing NP40. (a) 0.0021 g NP40/g polymer, (b) 0.0035 g NP40/g polymer, (c) 0.0154 g NP40/g polymer, (d) 0.0154 g NP40/g polymer, and (e) 0.0199 g NP40/g polymer.

peting processes that can occur when the latex surfactant level is adjusted. Plasticization augments fusion, while reduced interfacial energies hinder film fusion. The electron micrographs indicate increased fusion, suggesting that plasticization is the dominant process. However, careful examination reveals that the overall degree of coalescence does not seem to be greatly enhanced. Rather, there seems to be only a bridging of the particles in the interstitial region. It is likely that the high concentration of NP40 in the interstitial region has a plasticizing effect, as demonstrated by dynamic mechanical measurements. These results are in agreement with the work of Bradford and Vanderhoff,<sup>2,3</sup> since coalescence is enhanced when the polymer is plasticized (as expected), and NP40 appears to be compatible with acrylic copolymers. However, the performance of the films as barrier materials in coatings would likely not be improved, since the overall degree of film fusion is not increased.

The results described indicate that NaDBS and NP40 influence the film formation process differently. The difference in surfactant behavior is likely related to polymer/surfactant compatibility. The compatibility of NP40 and poly(methyl methacrylate-*co*-butyl acrylate) will be greater than that of NaDBS and the polymer because of the similarity in hydrophilicity. The results for NaDBS are in agreement with those of other authors,<sup>6,7</sup> since adsorption of NaDBS is unlikely to occur on the fairly polar surface of the copolymer containing methacrylic acid.

The results discussed here should not be extended, in general, to the two classes of surfactants

(i.e., anionic and nonionic). The influence of individual surfactant/polymer systems must be investigated individually. Although it is likely that the effect on viscoelastic properties is dominant over the effect on surface energetics, it is necessary to determine the degree to which an emulsifier will plasticize a particular polymer.

### Water Plasticization

The dynamic mechanical behavior of polymers L1 and L5 is illustrated in Figures 8 and 9. The data correspond to a strain frequency of  $1 \text{ rad} \times \text{s}^{-1}$ . At the strains selected for the experiments, all the materials exhibited linear viscoelasticity. The quality of the data is illustrated in Figure 10 by the overlap of the data obtained using three geometries.

All the materials show a plasticization effect when exposed to water for a prolonged period of time. The figures presented are representative of the copolymers synthesized. It was intended to compare the degree of water plasticization and the polymer structure (i.e., degree of crosslinking). Unfortunately, the plasticization effect is not truly quantifiable using dynamic mechanical testing, due to unavoidable experimental difficulties, which are detailed below.

In order to determine absolute values for the viscoelastic parameters, the water content of the specimens must be at an equilibrium value throughout the experiment. That is, the polymer sample must be fully saturated with water, and must remain so. For the parallel plate tests, the sample must be well adhered to the plates. This necessitates elevating

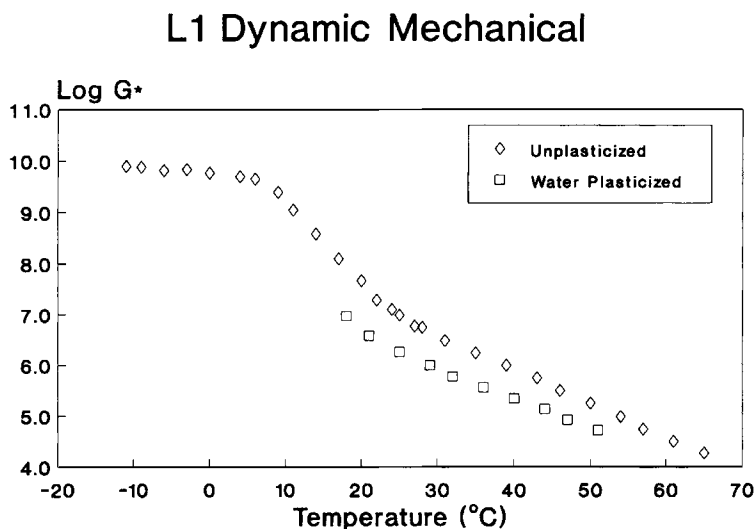


Figure 8

### L5 Dynamic Mechanical

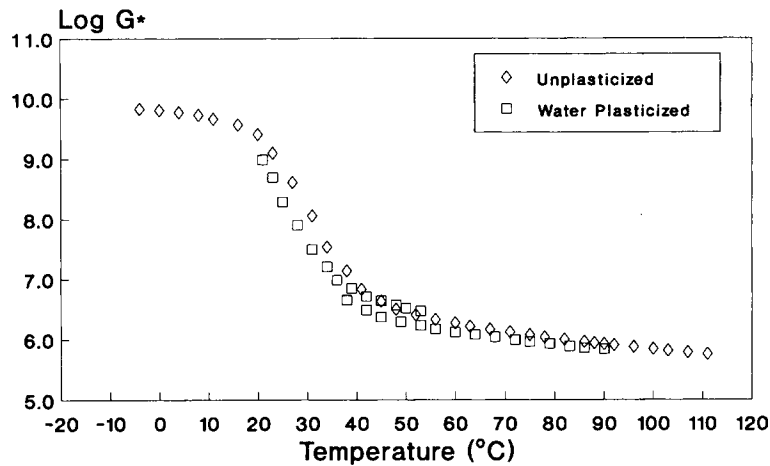


Figure 9

the temperature for several minutes. During this time, an unknown quantity of water will evaporate. Unfortunately, this cannot be compensated for by performing all the tests under identical conditions, as each material must be handled uniquely.

The two extremes that occur during film formation are represented in Figures 8 and 9. When the latex is prepared by emulsion polymerization, it is probable that the polymer contains the equilibrium water content, since the growing particle is always in contact with water. Subsequent storage, prior to incorporation in a coating, ensures that the polymer is water saturated. The slow kinetics of water dif-

fusion into the polymer are not likely to be applicable here. The other extreme corresponds to completely dry material (with reference to ambient conditions). This would correspond to the state of the polymer following stage III drying. It is likely that during stage I and early stage II that the polymer is saturated with water.

#### Effect of pH on Film Formation

The MFT, as a function of latex pH, is depicted in Figure 11. The scatter in the data occurred because each point corresponds to an individual measure-

### L3 Dynamic Mechanical

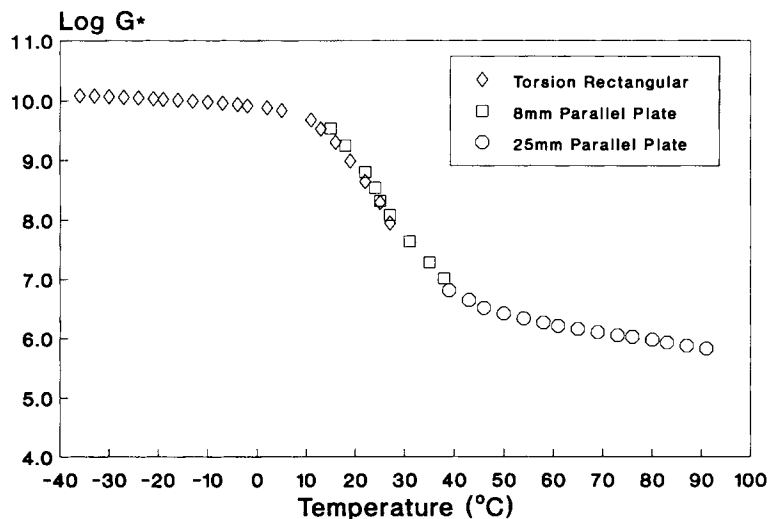


Figure 10

## MFT as a Function of pH, Latex L3

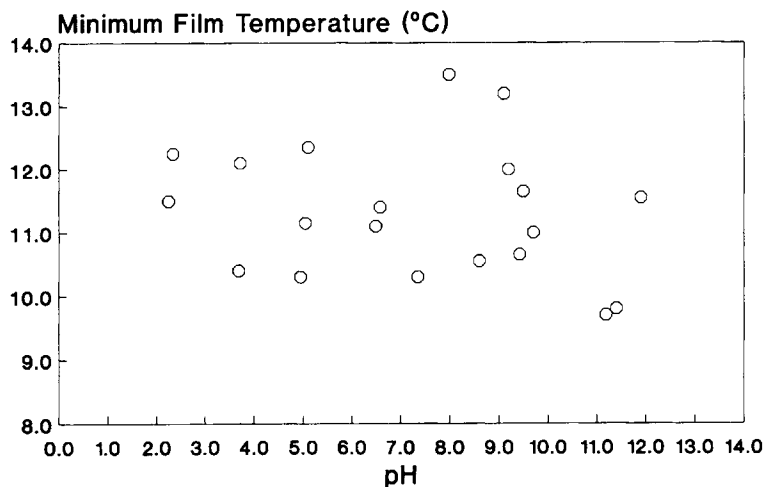


Figure 11

ment, rather than to the average of replicates usually shown in MFT plots. Figure 11 indicates that the MFT is independent of pH, a result not predicted by the work of Cogan.<sup>9</sup> One would expect that the carboxylic acid functionality on methacrylic acid would be neutralized by ammonium hydroxide, thus changing the character of the polymer. However, the quantity of methacrylic acid in the terpolymer (~ 2% by mass) is probably too small to be manifested.

The dramatic increase in MFT with increasing pH, observed by Cogan, is probably due to the conversion of a portion of PVAc to PVOH during polymerization. Thus, the effect seen by Cogan is really an effect of polymer modification that is particular to the polyvinyl acetate system. This type of effect is not expected here, and is not observed.

## CONCLUSIONS

Dynamic mechanical measurements indicated that poly(methyl methacrylate-*co*-butyl acrylate-*co*-methacrylic acid) is plasticized by NP40 surfactant. However, the NP40 content of the latex did not have an effect on the MFT. SEM revealed that a high NP40 concentration promotes film fusion locally in the interstitial regions, which is likely due to the plasticization of the polymer at the particle surfaces.

Film formation in the system containing NaDBS was shown to be independent of emulsifier concentration. Electron micrographs showed surface exudations.

The water plasticization of emulsion polymers produced via reactions containing crosslinking and chain transfer agents, was examined using a dynamic mechanical technique. All the materials studied were found to be plasticized by water. This effect is important in the film formation process, since the modulus and viscosity reduction accompanying plasticization can directly affect the degree of film coalescence.

The influence of pH on the film forming behavior of the poly(methyl methacrylate-*co*-butyl acrylate-*co*-methacrylic acid) system was studied. Measurements showed that the MFT is independent of pH.

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