

Effect of Carboxylic Monomers on Acid Distribution in Carboxylated Polystyrene Latices

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Synopsis

A study was made of the effect of carboxylic monomers, such as itaconic acid, acrylic acid, and methacrylic acid, on the relative distribution of acid in the aqueous serum phase to that on the latex surface to that buried in the particle of carboxylated polystyrene latices prepared by emulsion polymerization. The relative acid distribution of the carboxylated latices was determined by the conductometric titration method of Hen. Effect of carboxylic monomer levels and latex particle size on acid distribution ratio are given. It is shown that itaconic acid, being the most hydrophilic and having the least solubility in styrene, tends to distribute itself in favor of the aqueous serum phase, while acrylic acid, which has limited solubility in styrene and being sufficiently hydrophilic, tends to prefer the particle surface predominantly. Methacrylic acid, being the most hydrophobic of the three carboxylic monomers studied and having good solubility in styrene, is shown to be concentrated inside the particle core. The observed results are compared with other similar findings in the literature and analyzed in the light of accepted mechanisms for emulsion polymerization of carboxylated styrene systems.

INTRODUCTION

The introduction of carboxylic groups in the polymer chain of carboxylated latices has been found to result in the improvement of several significant properties¹⁻⁴ such as colloidal stability, mechanical and freeze-thaw stability, rheology, adhesion, etc. These properties of carboxylated latices are greatly influenced by the method of introduction and nature of the carboxylic monomer.^{5,6} This indicates that the distribution of acid groups in the system, namely, the relative distribution of acid in the serum phase to that on the latex surface to that buried in the latex core, is strongly dependent on polymerization conditions.

A few fundamental studies have been made on the behavior of carboxylic monomers in emulsion polymerization. It was shown by Fordyce and Ham⁷ that a considerable portion of itaconic acid is polymerized in the aqueous phase on emulsion polymerization with styrene. An electrophoretic study by Matsumoto and Shimada⁸ on emulsions of methyl methacrylate copolymers with acrylic and methacrylic acids has shown that acrylic acid concentrates preferentially at the particle surface, in contrast to methacrylic acid, which diffuses readily into the particle and copolymerizes with methyl methacrylate. Lately, several investigations⁹⁻¹² have been carried out on carboxylated latices to study the influence of the hydrophilic nature of growing radicals on particle formation and to examine the applicability of the homogeneous nucleation theory of emulsion polymerization¹³ to such systems.

In a carboxylated latex, the carboxylic acid group may be distributed in one of the three forms mentioned above (serum, surface, or buried in the latex).

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Several analytical techniques have been employed to determine this acid distribution. Potentiometric and conductometric titrations^{1,14,15} of latices and separated serums and ion-exchanged latices¹⁶ have been used to determine acid distribution in carboxylated latices. Green⁴ has used neutron activation analysis of oxygen and sodium to determine the total acid and turbidimetric titration of purified latex to determine the surface bound acid. Hen¹⁷ has shown that a simple conductometric back titration of alkali-treated carboxylated polystyrene gives satisfactory information on the acid distribution. Recently, Kangas¹⁸ used mixed solvents to determine the acid distribution by potentiometric and conductometric methods. However, the results obtained by the various methods agree only in a qualitative way due to differences in the method, time effects, handling of the samples, and somewhat arbitrary assignment of acids to the three loci.

In the present paper, the back titration method of Hen¹⁷ is used to study the effect of acrylic acid, itaconic acid, and methacrylic acid on the acid distribution in carboxylated polystyrene latices. The effect of the level of carboxylic monomers and particle size on the acid distribution is investigated. The observed results are explained in terms of the differences in the polymerization and solubility behavior of the three carboxylic monomers and literature findings on similar systems.

EXPERIMENTAL

Materials and Methods

Materials. Extrapure-grade styrene (St), acrylic acid (AA), methacrylic acid (MAA), and itaconic acid (IA) were used. Reagent-grade potassium persulfate was used as the initiator. Sodium lauryl sulfate from BDH Chemicals after purification was used as one of the surfactants. The other surfactant used was Aerosol AY (sodium diamyl sulfosuccinate) from American Cyanamid. Deionized water was used in all the experiments.

Emulsion Polymerization. A typical recipe is given in Table I. Emulsion polymerization was carried out at 50°C under nitrogen atmosphere using a batch process. Theoretical solids content in all the formulations was 25%, and generally the conversions were better than 98%. The acid comonomer content in the polymer was varied from 1% to 2% based on the total monomer.

Particle Size Determination. Particle size of the latices was determined using electron microscopy and Joyce-Loebl disc centrifuge sedimentation

TABLE I
Emulsion Polymerization Recipe

Monomers	500g
Surfactant	30 g Aerosol AY ^a or 17.4 g sodium lauryl sulfate ^b
K ₂ S ₂ O ₈	2.48 g
Distilled water	1575 g
Solids	25%
pH	about 3.0
Latex a series	Prepared with sodium lauryl sulfate
Latex B series	Prepared with Aerosol AY

^a American Cyanamid Product—sodium diamyl sulfosuccinate.

^b BDH product purified by ether extraction and recrystallization from water.

techniques. Latices (series A) made using sodium Lauryl sulfate as emulsifier were found to have a diameter of about 60 nm, while the ones prepared using Aerosol AY (series B) had a diameter of about 120 nm. In general, the particle size decreased with increase in the carboxylic comonomer content of the polymer in accordance with other findings.^{7,11}

Partition Coefficients of Carboxylic Comonomers. The determination of the partition coefficients of carboxylic comonomers was carried out as follows. To 100 cc water was added the prescribed amount of the carboxylic comonomer. After completion of dissolution, 100 cc St was introduced and stirred for 3 hr at 50°C (polymerization temperature). The aqueous and styrene phases were separated, and the acid content in each phase was determined by conductometric titration with 1N sodium hydroxide.

Ion Exchange of Latices. Some of the carboxylated latices were ion exchanged using purified mixed-bed Dowex resins according to the method of Vanderhoff.¹⁶ The ion-exchanged latices were titrated conductometrically against 1N NaOH to determine the carboxyl content of the latices.

Conductometric Titrations. Two kinds of conductometric titrations were performed using an automatic Metrohm titrimeter. The first type of conductometric titration, after Hen,¹⁷ is done by taking 2–3 g latex, adjusting the pH to 10.5 with 1N NaOH, and back titrating the excess against 1N H₂SO₄. The second method, after Vanderhoff,¹⁶ involves direct conductometric titration of ion-exchanged latices (1–2 g) against 1N NaOH. Due to the use of concentrated reagents for titration in an automated setup, the endpoints were quite sharp and the titer values were reproducible within 5–8 $\mu\text{eq/g}$ latex.

RESULTS AND DISCUSSION

Figure 1 shows a typical conductometric back titration curve obtained with carboxylated polystyrene latices. The overall features of the curve agree quite

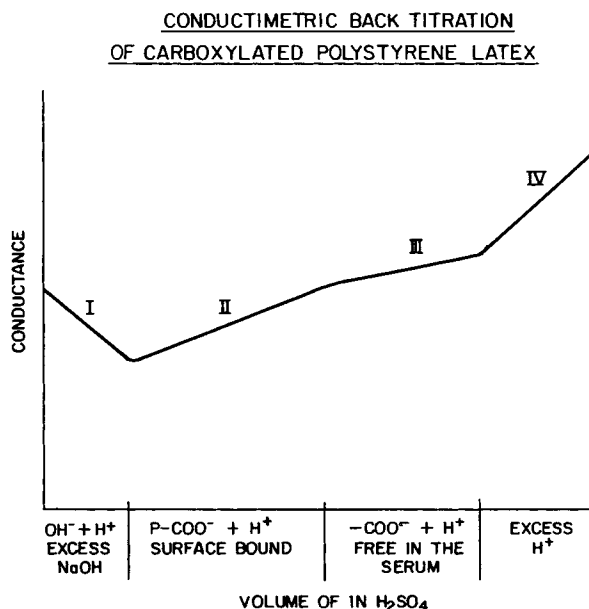


Fig. 1. Typical conductometric back titration curve of carboxylated polystyrene latex.

well with those reported by Hen.¹⁷ As explained by Hen, the curve has four distinct regions, with the first one (I) corresponding to the neutralization of excess NaOH, followed by another region (II) corresponding to the neutralization of surface-bound carboxylate groups. Regions III and IV correspond to the neutralization of free carboxylate groups in the serum and excess H_2SO_4 , respectively. Knowing the amount of surface-bound and serum-phase free carboxyl groups from such a titration, one can readily calculate the amount of carboxyl groups buried in the latex particle by material balance of the total acid content of the particular latex composition. Thus, one has a convenient way of determining the acid distribution in a carboxylated latex between latex surface, aqueous serum, and particle core.

The acid distribution thus estimated is only an arbitrary assignment. The acid distribution is found to change with the time (up to 1 hr, the distribution does not change) of alkali treatment, suggesting the swelling and diffusion of interior carboxyl groups as observed in alkali swelling of carboxylated latices.^{1,19} Preliminary data²⁰ indicate that this method could be used to study the rate of diffusion of interior carboxyl groups by monitoring the changes in acid content corresponding to the surface-bound region. It is also seen in preliminary investigations²⁰ that the back titration method does not work well with carboxylated acrylate and vinyl acetate systems due to complications arising from hydrolysis and saponification.

Figure 2 shows a typical curve corresponding to the direct titration of ion-exchanged carboxylated polystyrene latex. The first break is due to the protonated sulfate endgroups of the polymer molecules, and the second break corresponds to the carboxyl group of the acid comonomer.¹⁶ The carboxyl content determined by this method should closely correspond with the surface-bound acid determined as above by Hen's method.¹⁷

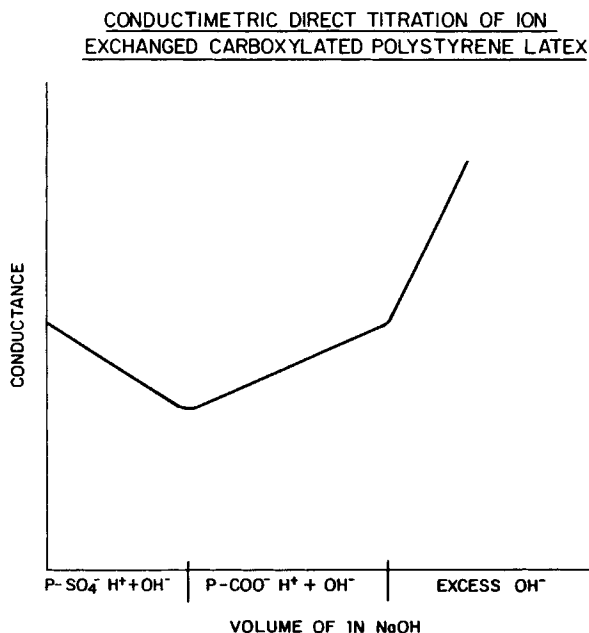


Fig. 2. Typical conductometric direct titration curve of ion-exchanged carboxylated polystyrene latex.

Results for the surface-bound carboxyl groups in carboxylated polystyrene latices as determined by Hen's back titration method and Vanderhoff's direct titration of ion-exchanged latices are shown in Table II. It is seen that the surface carboxyl content depends on the carboxylic monomer as determined by the two methods. We shall return to the differences in the behavior of the three carboxylic comonomers a little later. However, it is seen that the values for the surface-bound carboxyl groups determined by direct titration method are slightly lower than the corresponding values from the back titration method with all the three carboxylated latices studied. The lower values obtained with the direct method could be due to removal (desorption) of some of the loosely held acid by ion exchange resins. Another possibility is that in the back titration method the alkali has a longer time (5–10 min) to interact with the carboxyl groups on the surface as well as with some buried in the particle before the excess is back titrated, whereas in the direct titration method the neutralization time is quite rapid, probably involving only the surface carboxyl groups. This again indicates the arbitrariness of assigning the carboxyl groups to surface and buried loci. In any event, the agreement between the two methods is quite good, and the back titration method is quite satisfactory for comparing the differences in the distribution behavior of the three carboxylic monomers between surface, serum, and particle core loci of the carboxylated polystyrene latices.

Table III shows the distribution ratio of acid in the serum phase to that on the surface to that buried in the particle for the three carboxylated polystyrene latices at 1% and 2% carboxylic monomer levels. Several points are worth noting. It is seen that at both the acid levels studied, the amount of acid in the serum is highest with IA, followed by AA and MAA. At the 1% level, surface-bound acid is found to be higher for AA, followed by IA and MAA. MAA is found to have

TABLE II
Surface-Bound Carboxyl Groups in Carboxylated Polystyrene Latices

Latex ^a	μ eq. of Carboxyl groups/gram latex	
	Back titration method of Hen ¹⁷	Direct titration method of Vanderhoff ¹⁶
St/MAA	118	83
St/AA	154	130
St/IA	208	164

^a 2% Carboxylic comonomer prepared using purified sodium lauryl sulfate as surfactant (series A latices).

TABLE III
Effect of Carboxylic Monomer Level on Acid Distribution in Carboxylated Polystyrene Latices

Distribution loci in carboxylated polystyrene ^a	% of Acid at the three loci					
	1% Carboxylic monomer			2% Carboxylic monomer		
	IA	AA	MAA	IA	AA	MAA
Free in Serum	59	45	34	52	46	5
Surface bound	40	51	31	41	22	22
Buried in particle	1	4	35	7	32	73

^a Prepared using Aerosol AY (series B latices).

the highest buried acid, followed by AA, and there is very little buried acid with IA, in agreement with the observation of Hen.¹⁷ It is seen that the acid distribution ratio changes with the acid level somewhat differently in the three carboxylated systems. For instance, the distribution ratio is found to change such that serum-phase acid decreases quite dramatically with increase in acid level with MAA, while the surface-bound acid is affected somewhat with AA, and buried acid increases quite markedly with MAA. Carboxylic monomer level is seen to have very little effect on the acid distribution with IA copolymers.

The results presented here with AA and MAA agree qualitatively with the findings of Green⁴ and Kangas,¹⁸ who found that more acid was buried in the particle in MAA than in AA in carboxylated styrene-butadiene systems. Matsumoto and Shimada⁸ found that more MAA was buried in the methyl methacrylate latex particle compared to AA. However, the distribution ratio values obtained in this investigation are somewhat different from the values given by Green.⁴ Further, Green⁴ found very little effect of acid level on the distribution ratio, in contrast to our findings. These discrepancies could be due to differences in the polymerization conditions (they had used 25% neutralized acid compared to unneutralized acid in this study), monomer systems, particle size (see below), arbitrary assignment of distribution ratio depending on the method, etc. It is worth mentioning that Muroi¹ found from his studies on carboxylated ethyl acrylate latices that acid content corresponding to the serum phase and latex surface decreased with increase in the carboxylic comonomer content. Sakato and Okaya^{11,12} have found that the amount of acrylic acid in the range of 1%–5% affects the rate of emulsion polymerization and particle generation in St/AA systems due to the effect of the increased hydrophilic nature of growing radicals on the formation and stabilization of particles. These findings seem to support our observation that carboxylic monomer content affects the particle formation and acid distribution.

Let us look at the effect of particle size on the acid distribution ratio with the three carboxylic monomers at a carboxylic monomer level of 2%. The results are shown in Figure 3. The 60-nm-diameter (series A) and 120-nm-diameter (series B) latices were prepared, as mentioned above, with sodium lauryl sulfate and Aerosol AY surfactants, respectively. It is seen that particle size affects the acid distribution ratio differently with the three carboxylic monomers studied. It is seen that with IA and AA, as the particle size increases, the serum phase acid increases while the surface-bound acid decreases and the buried acid remains the same. These observations are in accord with those of Hen¹⁷ from his study on styrene/itaconic latices. In the case of methacrylic acid, it is seen that as the particle size increases, the already low amount of serum-phase acid is not affected. Further, with MAA, the surface-bound acid decreases whereas the buried acid increases dramatically with increase in particle size. It is rather straightforward to explain the decrease in surface-bound acid in all three cases with increase in particle size, as large particles have lower surface area. However, to explain other differences in the acid distribution ratio observed with the three carboxylic monomers, it is important to know the relative solubility of the three carboxylic monomers in St and water under polymerization conditions. The distribution coefficient of the three carboxylic monomers between St/water is discussed in the next section.

The partition coefficients of IA, AA, and MAA were determined by measuring the amount of the carboxylic monomer in the St and water phases on the as-

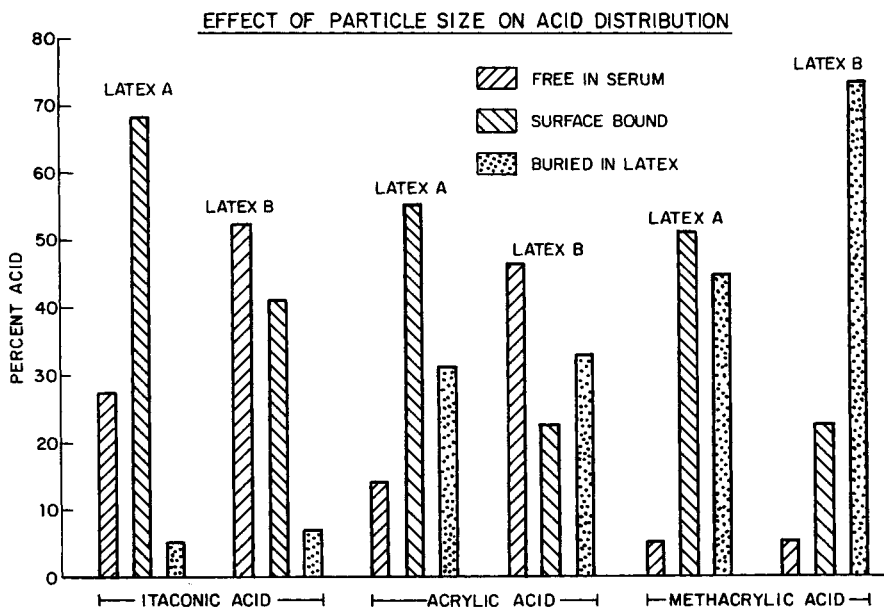


Fig. 3. Effect of particle size on acid distribution at 2% carboxylic monomer level. Latex A series of particle size 0.06 μ m and latex B series of particle size 0.14 μ m: (▨) free in serum; (▩) surface bound; (▤) buried in latex.

sumption that the association and dissociation of the carboxylic monomer can be neglected. The partition coefficients of IA, AA, and MAA between St/water at 50°C are shown in Table IV. It is seen that the solubility of the carboxylic acid monomers in styrene increases in the order MAA > AA > IA. The partition coefficient values reported here agree quite well with those reported in the literature for AA, MAA, and IA at 25°C^{6,8} and for IA at 70°C.⁷ The partition coefficient values indicate that IA (to a larger extent) and AA prefer to be in the aqueous phase while MAA tends to distribute itself preferentially in the styrene phase.

Now, let us examine whether we can explain the observed differences in the acid distribution ratio of IA, AA, and MAA monomers as a function of carboxylic monomer level and particle size of the copolymers. The results presented on the effect of acid level on the distribution ratio with the three carboxylic monomers show that the most hydrophilic IA (least solubility in St) is found to a large extent in the aqueous serum phase and on the particle surface with very little inside the particle. AA, which has limited solubility in St but being sufficiently hydrophilic, prefers the surface and latex core sites. MAA, which has the highest solubility in St and is least hydrophilic, prefers to be inside the particle core predominantly, with some on the latex surface and very little in the aqueous

TABLE IV
Distribution Coefficient of Carboxylic Comonomers Between Styrene and Water at 50°C

Carboxylic comonomer	Distribution coefficient
MAA	1.99
AA	0.20
IA	0.01

phase. The result shows that the amount of acid associated with the particle core and surface increases with the hydrophobic nature of the monomer, namely, $MAA > AA > IA$. The lower reactivity of IA as compared to AA or MAA must also be considered as a hindrance to its incorporation onto the latex particle.

Let us analyze the results on the effect of particle size on the acid distribution ratio with the three carboxylic monomers. We have already explained the observed decrease in surface-bound acid with increase in particle size. It is seen that the buried acid increases dramatically with MAA (44%–73%) compared to AA (31%–33%) and IA (5%–7%) as the particle size increased from 60 nm to 120 nm. It is known that the Aerosol AY used in preparing the larger-particle latex forms a larger micelle compared to sodium lauryl sulfate used in the preparation of 60-nm latices. Thus, the larger micelles in Aerosol AY latex recipes would readily solubilize more styrene compared to the sodium lauryl sulfate recipes. MAA, being more hydrophobic than IA and AA, would readily dissolve in the solubilized St in the micelle and thus end up in the particle core. IA and AA, being more water soluble, tend to remain in the aqueous phase; and, as the particle size increases, the serum-phase acid increases from 27% to 52% and from 14% to 46%, respectively, while the buried acid remains the same for IA and AA. It is seen that the serum-phase acid for the hydrophobic MAA does not change with particle size. Thus, once again we see the effect of monomer partition coefficient between St and water on the acid distribution ratio in the carboxylated latices.

The data indicate that the monomer diffusion mechanism is important. As the carboxyl monomer becomes more hydrophobic, it can diffuse readily into the growing particle, polymerize, and thus become part of a particle core more readily than the hydrophilic monomer such as IA, which must wait to be carried to the particle surface by means of oligomeric radicals formed in the aqueous phase. Ceska⁹ in his studies on polymerization rates in the presence of carboxylic monomers found that the rates fell in the order $MAA > AA > IA$. He discounted the importance of aqueous oligomeric diffusion in explaining his experimental results. Recent work^{11,12} on the elucidation of emulsion polymerization mechanisms in carboxylated styrene systems has shown that at high surfactant concentrations (greater than $6mM$ for sodium lauryl sulfate) and in the presence of undissociated acids at low acid levels (both conditions satisfied in our study), the Smith-Ewart-type mechanism is still valid for the emulsion polymerization of carboxylated styrene systems, in preference to the homogeneous nucleation theory.¹³ According to the Smith-Ewart model,²¹ the active site is the micelle and the monomer solubilized in it. Hence, the relative solubility of carboxylic comonomers in styrene compared to water is important in the emulsion copolymerization of carboxylated styrene systems. This is in agreement with the observation of Fordyce and Ham⁷ who found that IA did not copolymerize readily with St by emulsion techniques but did so quite readily in solution polymerization. They explained this as being due to the low solubility of IA in St and that in emulsion polymerization the reaction proceeds within the oil droplet or at its interface.

Thus, our findings on the effect of carboxylic monomers on the relative distribution of acid groups in the serum phase to that on the latex surface to that buried in the latex core in carboxylated polystyrene systems, determined by the simple conductometric method of Hen,¹⁷ are in agreement with other findings in the literature, as well as with the accepted emulsion polymerization mechanism of styrene in the presence of minor amounts of a carboxylic monomer.

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References

1. S. Muroi, *J. Appl. Polym. Sci.*, **10**, 713 (1966).
2. S. Muroi, K. Hosoi, and T. Ishikawa, *J. Appl. Polym. Sci.*, **11**, 1963 (1967).
3. D. C. Blackley, *High Polymer Latices*, Maclaren, London, 1966.
4. B. W. Green, *J. Colloid Interface Sci.*, **43**, 449, 462 (1973).
5. G. L. Meier (to Dow Chemical Co.), U.S. Pat. 3,575,913 (1971).
6. K. Sakota and T. Okaya, *J. Appl. Polym. Sci.*, **20**, 2583 (1976).
7. R. G. Fordyce and G. G. Ham, *J. Am. Chem. Soc.*, **69**, 695 (1947).
8. T. Matsumoto and M. Shimada, *Kobunshi Kagaku*, **22**, 172 (1965).
9. G. W. Ceska, *J. Appl. Polym. Sci.*, **18**, 427 (1974).
10. G. W. Ceska, *J. Appl. Polym. Sci.*, **18**, 2493 (1974).
11. K. Sakota and T. Okaya, *J. Appl. Polym. Sci.*, **20**, 3255 (1976).
12. K. Sakota and T. Okaya, *J. Appl. Polym. Sci.*, **20**, 3265 (1976).
13. R. M. Fitch and C. H. Tsai, *Polymer Colloids*, Plenum Press, New York, 1971.
14. J. Hearn, R. H. Ottewill, and J. N. Shaw, *Br. Polym. J.*, **2**, 122 (1970).
15. S. Muroi and K. Hosoi, *Kobunshi Kagaku*, **26**, 416, (1969).
16. H. J. Van den Hul and J. W. Vanderhoff, *Br. Polym. J.*, **2**, 121 (1970).
17. J. Hen, *J. Colloid Interface Sci.*, **49**, 425 (1974).
18. D. A. Kangas, *Coatings Plast. Prepr.*, 172nd ACS Meeting, **36** (No. 2), 353 (1976).
19. H. Wesslaw, *Makromol. Chem.*, **69**, 220 (1963).
20. B. R. Vijayendran, unpublished work.
21. W. W. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).

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