



Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and
subscription information:

<http://www.tandfonline.com/loi/gmcl17>

The Morphology of Emulsion Polymerized Latex Particlest

G. D. Wignall ^a, V. R. Ramakrishnan ^{a e}, M. A. Linne ^{b f}, A. Klein ^b,
L. H. Sperling ^b, M. P. Wai ^c, R. A. Gelman ^c, M. G. Fatica ^c, R. H.
Hoerl ^c, L. W. Fisher ^d, S. M. Melpolder ^g & J. M. O'Reilly ^g

^a National Center for Small-Angle Scattering Research, Oak Ridge
National Laboratory, Oak Ridge, Tennessee, 37831

^b Polymer Science and Engineering Program, Lehigh University,
Bethlehem, Pennsylvania, 18015

^c Hercules Research Center, Wilmington, DE, 19894

^d Analytical Technology Division, Eastman Kodak Company,
Rochester, New York, 14650

^e Brookhaven National Laboratory, Upton, NY, 11973

^f Dow Chemical Corporation, Midland, MI.

^g Corporate Research Laboratories, Eastman Kodak Company,
Rochester, New York, 14650

Version of record first published: 22 Sep 2006.

To cite this article: G. D. Wignall , V. R. Ramakrishnan , M. A. Linne , A. Klein , L. H. Sperling , M. P. Wai , R. A. Gelman , M. G. Fatica , R. H. Hoerl , L. W. Fisher , S. M. Melpolder & J. M. O'Reilly (1990): The Morphology of Emulsion Polymerized Latex Particlest, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 180:1, 25-39

To link to this article: <http://dx.doi.org/10.1080/00268949008025784>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings,

demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., 1990, Vol. 180A, pp. 25–39
Reprints available directly from the publisher
Photocopying permitted by license only
© 1990 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

The Morphology of Emulsion Polymerized Latex Particles†

G. D. WIGNALL¹ and V. R. RAMAKRISHNAN²

National Center for Small-Angle Scattering Research, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

M. A. LINNE,³ A. KLEIN and L. H. SPERLING

Polymer Science and Engineering Program, Lehigh University, Bethlehem, Pennsylvania 18015

M. P. WAI, R. A. GELMAN, M. G. FATICA and R. H. HOERL

Hercules Research Center, Wilmington, DE 19894

L. W. FISHER,§ S. M. MELPOLDER⁺ and J. M. O'REILLY⁺

§Analytical Technology Division and ⁺Corporate Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

Under monomer starved feed conditions, emulsion polymerization of perdeuterated methyl methacrylate and styrene in the presence of preformed polymethylmethacrylate latexes resulted in particles with a core-shell morphology, as determined by small-angle neutron scattering (SANS) analysis for a hollow sphere. The locus of polymerization of the added deuterated monomer is therefore at the particle surface. In similar measurements a statistical copolymer of styrene and methyl methacrylate was used as seed particles for further polymerization of trideuteromethyl methacrylate. The resulting polymer latex was again shown to have a core-shell morphological structure as determined by SANS. In both studies the overall size of the particle was in excellent agreement with the values obtained by other techniques (light-scattering, transmission electron microscopy, etc.). SANS experiments were also undertaken on polystyrene latexes polymerized by equilibrium swelling methods, with deuterated polymer forming the first or second step. The experiments covered a molecular weight range $6 \times 10^4 < M < 6 \times 10^6$ g/mol. For $M > 10^6$ the molecular weights determined via SANS and also by gel permeation chromatography (GPC) are consistent with the experimental errors, indicating that the deuterium labeled molecular are randomly distributed in the latex. These results led to the finding that the polymer chains were constrained in the latex particles by factors of 2–4 from the relaxed coil dimensions. For $M < 10^6$ g/mol SANS gave zero angle scattering intensities much higher than expected on the basis of a random distribution of labeled molecules. Several models were examined, including the possible development of core-shell structures at lower molecular weights.

†Research supported by Hercules Incorporated, Eastman Kodak Company, and the National Science Foundation through Grant No. CBT-8512923; and under grant DMR-8616912, with the Division of Materials Science, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

¹To whom correspondence should be addressed.

²Current address: Brookhaven National Laboratory, Upton, NY 11973.

³Current address: Dow Chemical Corporation, Midland, MI.

INTRODUCTION

Latexes constitute one of the most important forms of polymers, which currently account for about 20% of all synthetic polymers consumed. Such latexes are widely used in the coating industries as well as in engineering applications. Many properties of latex polymers originate in the molecular conformation and structure of the polymer chains inside the latex particles, though there is no general agreement on the actual structure of the latex. Because the latex interacts with its environment through its surfaces, understanding and control of the surface properties are particularly important. In the 1970's Grancio and Williams¹ postulated a polymer-rich spherical core surrounded by a monomer-rich shell which serves as the major locus of polymerization, thus giving rise to a core-shell morphology. This model, in which the first formed polymer constitutes the core and the second formed polymer makes up the shell has received much support but also significant criticism and the same evidence was often used to support conflicting viewpoints. The current interest in latexes requires characterization techniques that probe the internal structure of latex particles. With latex particle diameters on the order of 1000 Å, light and small-angle x-ray scattering may be used to measure intraparticle dimensions. Since the early 1980's neutron scattering has been used in combination with contrast variation methods to isotopically label particular chains generated at specific points in the polymerization process.²⁻⁸ The scattering contrast between normal (H-labeled) and perdeuterated (D-labeled) molecules allows the locations and dimensions of the deuterium labeled chains to be determined. This paper summarizes the results of three independent studies^{2,3,4} of the morphology of emulsion-polymerized latexes undertaken on the small-angle neutron scattering (SANS) facilities of the National Center for Small-Angle Scattering Research (NCSASR). Two studies^{2,3} confirmed that core-shell structure is generated under monomer starved conditions where the rates of monomer addition and polymerization are equal. These experiments were conducted both on polymethylmethacrylate (PMMA) latexes (PMMAH latex cores with PMMA or polystyrene-D shells) and also on copolymer systems (PSH-co-PMMAH latex cores with PMMA shells). Work currently in progress⁴ centers on the measurement of the molecular dimensions of very large chains within small latex particles. For obvious reasons the molecular dimensions can only be measured if the labeled/deuterated chains are statistically distributed in the system. For this work the latexes were prepared by swelling to equilibrium a seed latex (H- or D-polystyrene (PS) in contrasting monomer (D- or H-styrene) and then continuing the polymerization to completion.

Latex preparation

(a) *Monomer-starved polymerizations.* Both homopolymer and copolymer latexes were synthesized and examined by SANS. Polymethylmethacrylate (PMMA) core latexes were synthesized by conventional batch emulsion polymerization.³ The reaction mixtures were exhaustively degassed, and polymerizations were run under nitrogen at 90°C. Core C1 was prepared in water, and 25/75 wt % H₂O/D₂O was used as the reaction medium for cores C2 and C3. Potassium persulfate was used as the initiator at a level of 1% based on monomer. Triton 770 was used as surfactant

at concentrations of 1% for cores C1 and C2 and 2% for core C3. Reactions were allowed to proceed for ~ 5 h, with final solids' contents being $\sim 15\%$. Light scattering of the PMMA latexes was measured on a Sofica model 42000 photometer. Average particle sizes were calculated from the ratio of scattering intensities at 135° and 45° by the use of theoretical Mie scattering functions. In a second synthetic step, 98% perdeuterated styrene (D-S) or 99% perdeuterated methyl methacrylate (DMMA) was polymerized in the presence of a 15 mL aliquot of the PMMA latex C1, described above. For most of these polymerizations, the deuterated monomer was added during the reaction at a rate of 0.3 mL/min, and the mixtures were kept at the reaction temperature for 1 h after monomer addition was completed. For sample S1-D, the total monomer charge was added to the reaction vessel at the beginning of the second polymerization.

Seed latex copolymers of 49/51 mol ratio poly(styrene-co-methylmethacrylate) were synthesized using styrene and methylmethacrylate. Polymerizations were conducted in a 0.5 liter cylindrical jacketed reaction flask equipped with reflux condenser. To the nitrogen-purged reactor, 210 g water, 0.12 g sodium lauryl sulphate and 0.05 g initiator (ammonium peroxydisulphate) were charged. The contents were purged with nitrogen, while stirring, and the temperature was brought to 70°C over 20 min. A monomer mixture, 25 g each of styrene and methyl methacrylate, was next added to the reactor simultaneously with a separate addition of 0.19 g of sodium lauryl sulphate and 0.015 g initiator dissolved in 50 g of water. Both feeds were added to the reactor at constant rates over 20 min. When the addition was complete, 0.2 g initiator was added to the reactor and the temperature maintained with stirring for an additional 30 min. To the reactor set-up as described above, 105 g of seed (core) latex (16.2% total solids) was charged. The seed latex was brought to 70°C with stirring and nitrogen purge. Methyl- d_3 methacrylate (17 g) was added next over 8 min. The latex was maintained at 70°C with stirring for an additional 30 min, then cooled immediately.

(b) *Equilibrium swelling polymerizations.* The latex composition for SANS analysis was 50/50 mol % of polydeuterostyrene and polyprotostyrene. This molar ratio yields the highest scattering intensities for single chain SANS determination.⁹ The synthetic route utilized a seed latex of either polyprotostyrene (PSH) or polydeuterostyrene (PSD). This seed latex was then swollen overnight to equilibrium with the counterpart monomer. The polymerization was then continued to completion under the seed polymerization conditions. For each experiment an appropriate blank was synthesized. However, the seed was a 50/50 mol % statistical copolymer of P-S and D-S. The blank seed was reswollen with the same monomer mixture, simulating the actual sample synthesis. After equilibrium the latex blank was allowed to polymerize to completion. Gravimetric analysis of both seed and final latex demonstrated nearly complete conversion of the monomer, $> 98\%$. The polymerizations were executed in bottles at 50 or 60°C , to obtain the desired particle size range.^{10,11} Carbon tetrachloride was used as a chain transfer agent to vary the molecular weight from ultra high ($\approx 6 \times 10^6$ g/mol) to medium values ($\approx 6 \times 10^4$ g/mol) without significantly changing the particle size distribution. Weight averaged molecular weights (M_w) of the chains were measured by SANS and also by gel permeation chromatography (GPC). The ratio of these two quantities should equal

unity within the experimental errors and any departure from this value is an indication that the labeled molecules are not randomly distributed in the latex. Three different polymerization recipes¹⁰ were used to vary the concentrations of initiator, (potassium persulphate) chain transfer agent (CCl_4) surfactant and pH regulator (sodium bicarbonate).

Small-angle neutron scattering

The neutron experiments were performed on the 30-m small-angle neutron scattering facility at the National Center for Small-Angle Scattering Research, Oak Ridge National Laboratory. A description of the apparatus has been published elsewhere.¹² The incident beam of wavelength $\lambda = 4.75 \text{ \AA}$ was collimated by a source slit (1.7 cm diameter) and a sample slit (0.9 cm diameter), separated by a distance of 7.6 m. The area detector ($64 \times 64 \text{ cm}^2$) was placed at a sample-to-detector distance (SDD) of 18.9 m. This gives a scattering vector (Q) = $4 \pi \lambda^{-1} \sin \theta$ range of $3 \times 10^{-3} < Q < 3 \times 10^{-2} \text{ \AA}^{-1}$ where 2θ is the angle of scattering. Typical runs consisted of sample scattering and then correction for instrumental background, parasitic scattering and detector sensitivity. Calibration of the data was accomplished by means of precalibrated standards.¹³ The data were converted to an absolute differential scattering cross section per unit solid angle per unit volume, $d\Sigma(q)/d\Omega$, in units of cm^{-1} . All samples showed cylindrical symmetry about the incident beam and the data were radially averaged. In view of the large particle size of the latexes studied, it is important to consider instrumental resolution effects resulting from the finite resolution of the detector elements, the wavelength spread of the incident beam ($\Delta\lambda/\lambda \sim 6\%$) and the angular divergence of the incident and scattered beams determined by the sizes of the sample and source slits. The mathematical procedures for the desmearing process have been discussed by Glatter^{14,15} and Moore.¹⁶ The algorithm used here was the one developed by Moore¹⁶ and applied to the particular geometry of the 30 m instrument by Ramakrishnan.¹⁷ In addition to giving the desmeared intensity curve, the method, gives the radius of gyration R_g , the zero-angle cross section $d\Sigma(O)/d\Omega$, and the maximum dimensions of the particles even though data were not collected in the true Guinier range ($QR_g < 1$). These parameters agree very well with the values obtained by other methods. The PMMAH latex cores were suspended in $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures with concentrations of 65–73 vol % D_2O . The PMMAH-PMMA and PMMAH-PSD latexes were run in $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures chosen to match the scattering length densities (SLD) of the PMMAH core (27 vol % D_2O). For the polystyrene-co-MMA random copolymer latexes, the cores were run in pure D_2O while the shells were run in 23 vol % D_2O , which again matches, the SLD of the core. The PSH-PSD samples were run in 64.5 vol % D_2O mixtures. At this concentration the SLD of the aqueous phase matches the average SLD of the latex. Thus if the labeled molecules are randomly distributed in the latex the scattering due to the latex particle shape vanishes, leaving only the component due to the individual labeled molecules within the latex.¹⁰ The experiments employed the concentrations of latex particles (ϕ) in the range $0.25 < \phi < 10 \text{ vol \%}$.^{18,19} The justification for using such high particle concentrations is discussed in subsequent sections.

Analysis of SANS data: I latexes polymerized under monomer starved conditions

For a homogeneous particle, the neutron scattering cross section is given by

$$\frac{d\Sigma}{d\Omega}(Q) = (\rho_m - \rho_p)^2 N_p V_p^2 P(Q) \quad (1)$$

where ρ_m and ρ_p are the scattering densities of the medium and the particle, respectively, N_p is the number of particles per unit volume, V_p is the particle volume, $P(Q)$ is the particle form factor. For a solid sphere of uniform radius $P(Q)$ is given by²⁰

$$P(Q) = \frac{9(\sin QR - QR \cos QR)^2}{(Q^3 R^3)^2} \quad (2)$$

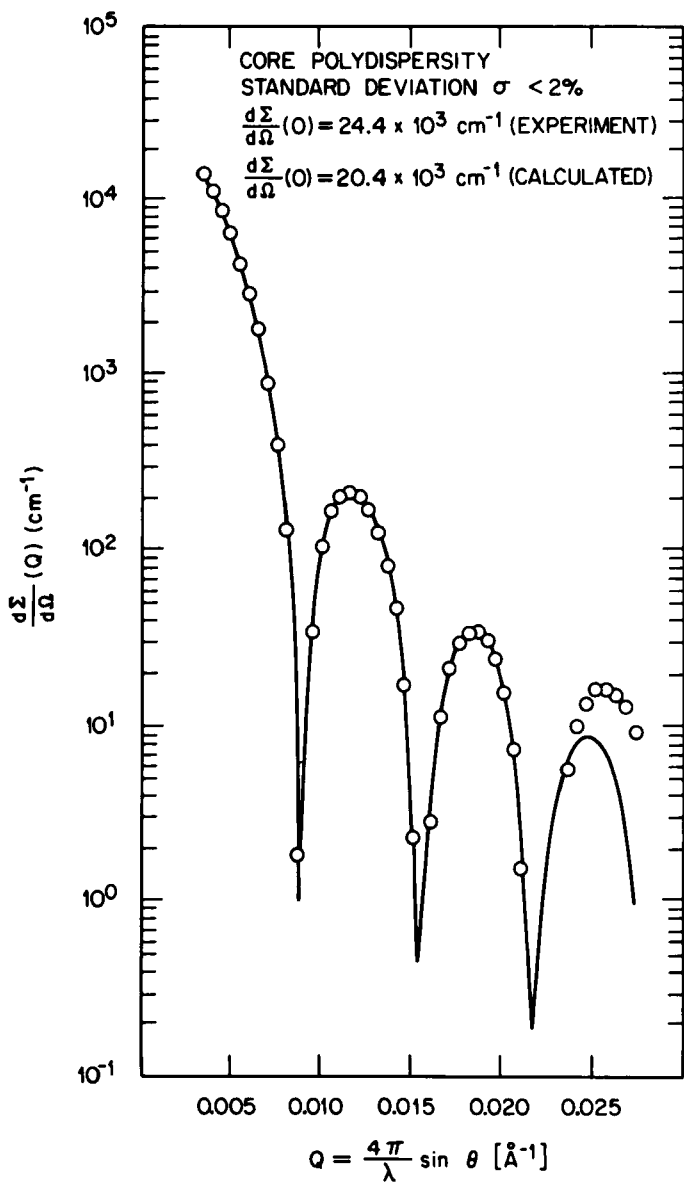
The particle form factor that describes the angular dependence of scattering intensity from a hollow sphere of uniform scattering density is given by Pecora and Aragon,²¹ as

$$P(Q) = \left[\frac{3}{Q^3 R^3 (1 - \ell^3)} (\sin(QR) - \sin(RQ\ell) - QR \cos(QR) + QR\ell \cos(QR\ell)) \right]^2 \quad (3)$$

where $\ell = a/R$, and R and a are the outer and inner radii, respectively. At $\ell = 0$, this hollow-sphere scattering function reduces to the solid-sphere scattering function. The number of maxima and minima in the scattering curve for homogeneous spherical particles within a given angular range increases with particle size. Analysis of extrema positions is a useful approach for the determination of particle size, and particle radii associated with the extrema positions can be calculated from analytical expressions.³ For the polymer latex samples investigated, extrema positions were independent of latex concentrations and were not shifted by the contribution to the total scattering by the continuous phase. The radii calculated from the extrema positions³ for the three PMMA cores (495, 615, and 470 Å are close to the values 490, 615, and 475 Å determined by the angle-ratio, light-scattering method for cores C1, C2, and C3, respectively. The corrected SANS patterns for cores C1 (Figure 1) and C2 compare reasonably well with theoretical curves for monodisperse spheres both in shape and in the absolute intensity (see below). Particle Size variations in latex samples are often described by the zero-order logarithmic (ZOLD) distribution.²² For this distribution, the frequency of particles of radius R is given by

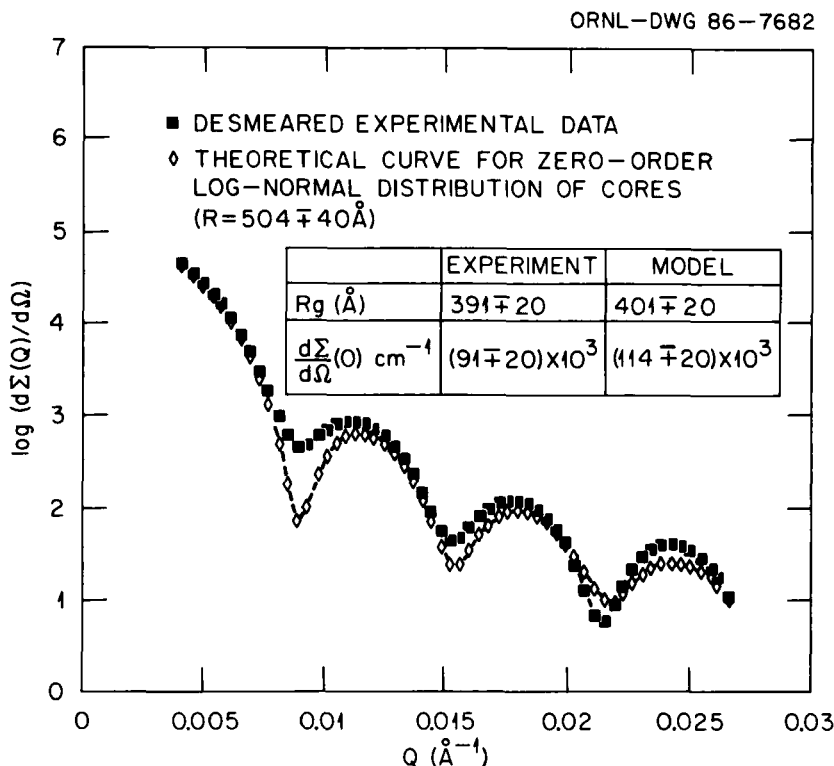
$$g(R) = \frac{\exp - \left[\frac{(\ell_n R - \ell_n R_m)^2}{2\sigma_0^2} \right]}{(2\pi)^{1/2} \sigma_0 R_m \exp(\sigma_0^2/2)} \quad (4)$$

ORNL-DWG 83-9891



Comparison Of Desmeared Sans Data (O) For PMMA
 Latex C1 (4.0 vol %) With Theoretical Scattering
 For Sphere Of Radius 495 Å
 (Radius By Light Scattering = 490 Å)

FIGURE 1



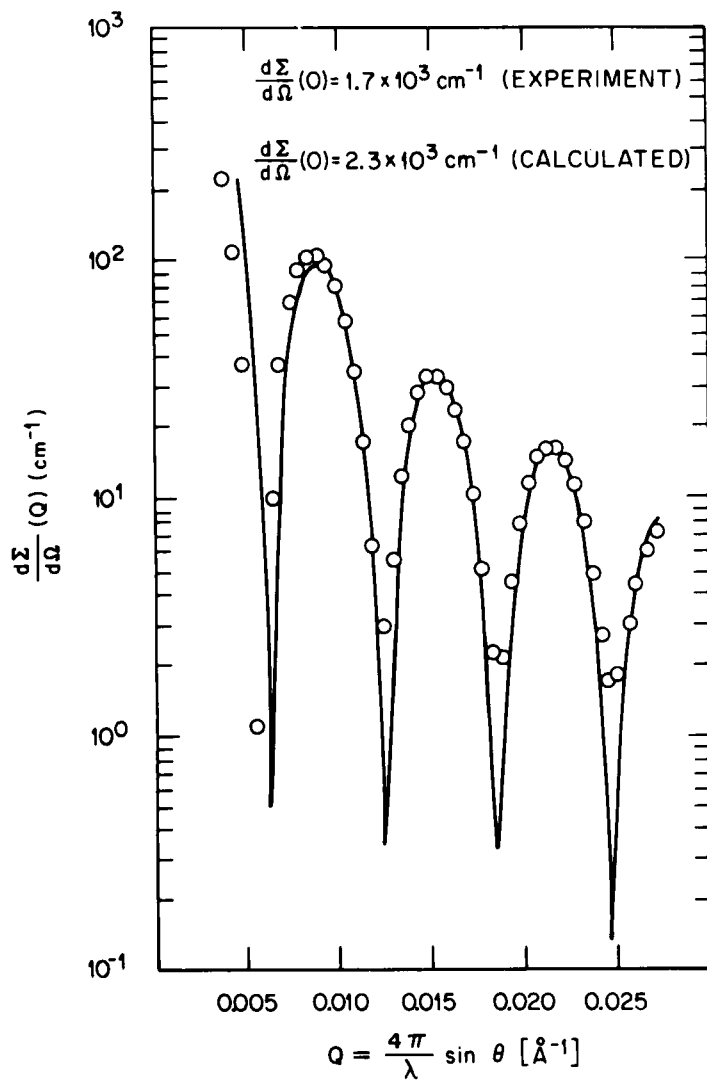
Comparison of Experimental SANS data and Theoretical Scattering Function for PS-PMMA Core Latexes in D_2O .

FIGURE 2

where R_m is the modal radius and σ_0 is a measure of the width of distribution and is related to the standard deviation σ as follows:

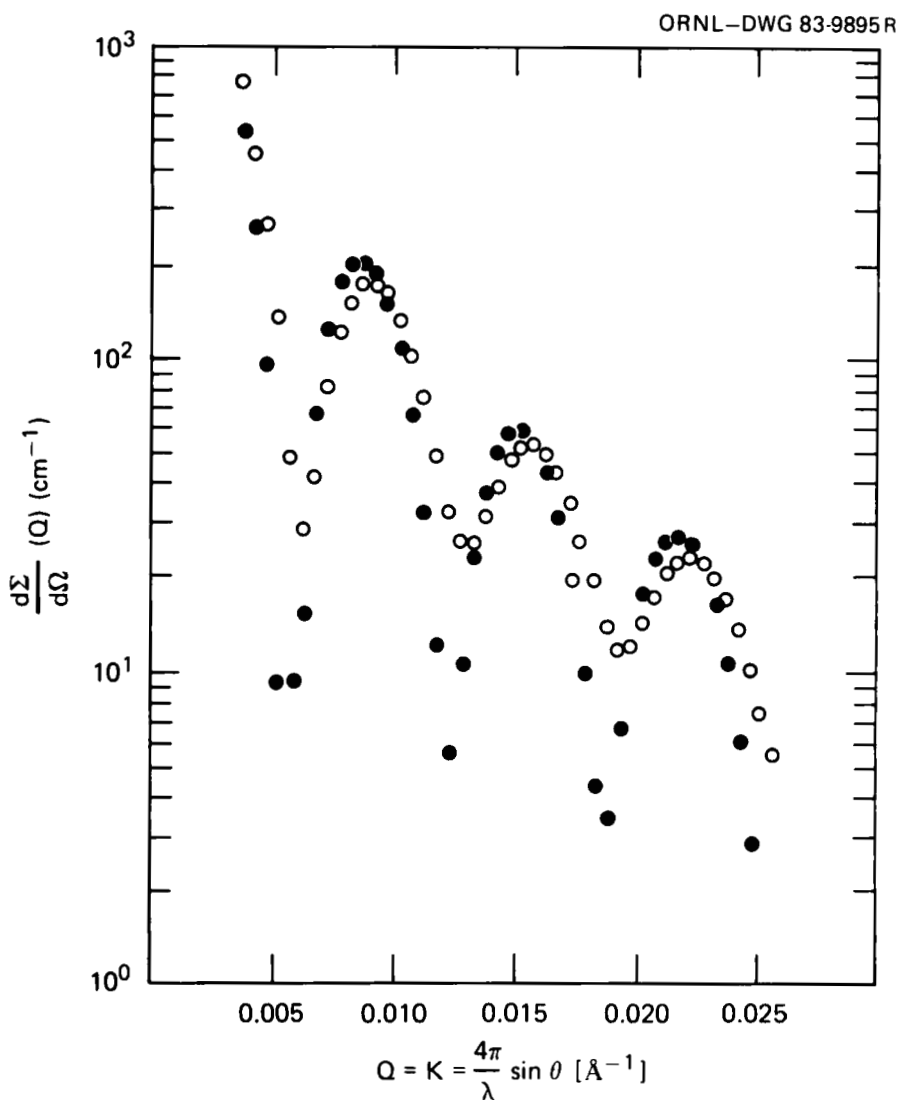
$$\sigma = R_m [\exp(4\sigma_0^2) - \exp(3\sigma_0^2)]^{1/2} \quad (5)$$

Standard deviations of the PMMA latexes were estimated from the depths of the minima in the scattering curve to be $< 2\%$. Figure 2 shows desmeared SANS data for the copolymer core compared to the solid sphere scattering function (Equation 2) using the ZOLD in the average diameter $\bar{D} = 1010 \pm 92$ Å. Figure 3 shows the experimental SANS data for a sample based on core C1 with a PMMA shell. The data are compared to the hollow sphere scattering function with an inner radius of 495 Å and a shell 30 Å thick. The fit of these experimental data is reasonable but not quite as good as that observed for the cores. The depth and breadth of these experimental minima could be due to some increase in polydispersity or deviations from sphericity and some interpenetration of core and shell polymer may have occurred. Use of deuterated methylmethacrylate and deuterated styrene



Desmeared SANS Data (O) For PMMA Latex C1 (4.6 vol %) With 30 Å D-DMMA Shell On Surface (Core Contrast Matched) Compared With Theoretical Hollow Shell Scattering

FIGURE 3



**DESMEARED SANS DATA FOR PMMA-H CORE WITH PSD-SHELL (○)
AND PMMA-D SHELL (●). CORE CONTRAST MATCHED IN H₂O/D₂O.**

FIGURE 4

in the second polymerization step allows one to analyze differences in particle morphology for compatible and incompatible polymer pairs, respectively. Figure 4 shows the corresponding desmeared neutron-scattering patterns for these samples. Polymer incompatibility produces a “raspberry-like” surface morphology for the PMMAH-PSD latex composite. The greater polydispersity of shell thickness in this

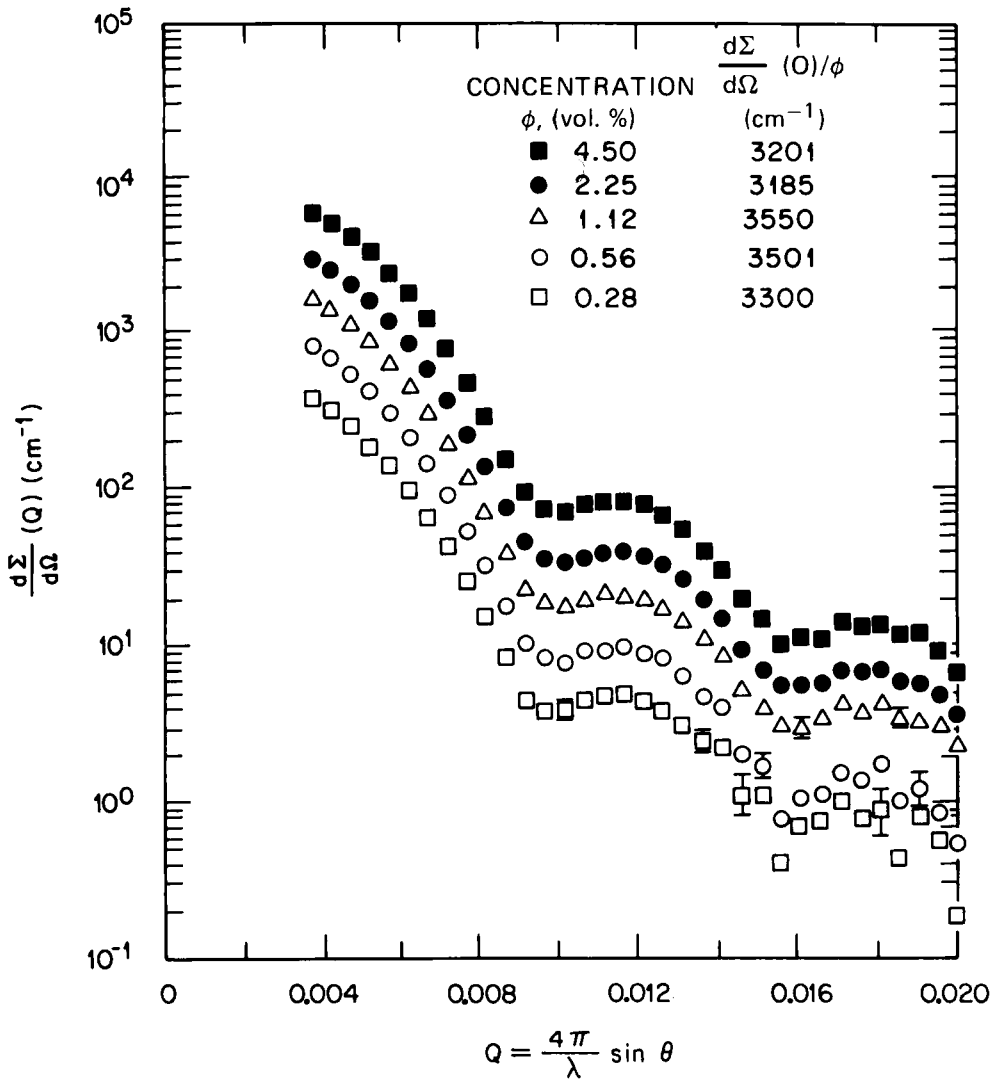
TABLE I
Measured and Calculated Absolute Cross Sections for Latex Suspensions and Comparison of SANS
Dimensions With Other Techniques

Latex	Type		$\phi(\%)$	vol% D_2O	$d\Sigma(O)$ Observed ($\pm 15\%$)	$(\text{cm}^{-1}) \times 10^{-3}$ Calculated ($\pm 15\%$)	Average Diameter $D(\text{\AA})$		
	Core	Shell					SANS	LS	TEM
C1	PMMAH		1.1	65.0	4.0	4.7			
C1	PMMAH		1.9	73.0	12.4	11.8	990	980	
C1	PMMAH		3.9	73.0	19.3	23.6			
C1	PMMAH		4.0	69.1	24.3	20.4			
C2	PMMAH		7.5	68.2	45.0	68.5	1230	1230	
SIA	PMMAH	PMMAD	9.4	26.8	4.2	5.4			
SIB	PMMAH	PSD	10.3	26.8	4.0	4.6			
SID	PMMAH	PMMAD	4.6	26.8	1.7	2.3	1056	1060	
A	PSH-co-PMMA		9.3	23.0	91.0	114	1010	1120	900
B	PS-co-PMMA	PMMAD3	9.0	23.0	14.0	12.6	1200	1300	1070

sample relative to the PMMAH-PMMAD latex is evident in the respective scattering curves.

In addition to the shape of the scattering envelope, the scattering intensity provides an independent check on the size of the concentration of particles and the scattering length density are known. The absolute intensity at zero scattering angle is given by Equation (1) with $P(O) = 1$. For the core, V_p is the volume of the latex particle in solution. For the shells, a core-shell structure was assumed for the absolute intensity calculations and V_p was taken to be the volume of the labeled polymer in the shell. The core and solution scattering length densities were matched (i.e., the core contrast was zero). The measured and calculated absolute cross sections are shown in Table I. All the measured cross sections are within 35% of the calculated values and the majority are within $\pm 20\%$. As mentioned above the experiments employed relatively high concentrations of latex particles ($\phi \sim 0.25 - 10$ vol %) in order to increase the signal-to-noise-ratio of the experiment and also because concentration studies (Figure 5) have indicated that the $d\Sigma(O)/d\Omega$ is proportional to ϕ in this range. Such behavior is quite surprising in view of the known tendency of neutral particles to form correlated structures in concentrated solutions.¹⁸ Calculations indicate that excluded volume effects alone should perturb the radius of gyration and zero angle cross section measured via SANS by $\approx 10\%$ for even a 1% volume fraction of particles.¹⁹ We believe that there are two reasons for the success of the above studies using relatively large volume fractions of latexes. Firstly, the above estimates of the perturbations to R_g and $d\Sigma(Q)/d\Omega$ refer to data analyzed only in the low Q region via Zimm or Guinier analysis. In contrast to this, the previous^{2,3} studies used indirect Fourier transform methods,¹⁷ which make use of data in the whole measured Q -range. This makes the analysis much less sensitive to concentration effects which are exhibited predominantly at low Q making R_g and $d\Sigma(O)/d\Omega$ virtually independent of concentration in the range studied (Figure 5). A second reason for this behavior is illustrated in Figure 6(a) which

ORNL-DWG 83-9906



$\frac{d\Sigma}{d\Omega} (Q)$ vs For Various Concentrations Of PMMA
Latexes in 65:35 vol % Mixture Of D₂O/H₂O

FIGURE 5

shows estimates of the excluded volume effect in concentrated ($\phi \approx 0.1$) latex solutions.¹⁸ In the absence of excluded volume effects the cross section is given by Equation (1). The effect of excluded volume interactions is to replace $P(Q)$ in Equation (1) by the product $P(Q)S(Q)$ where $S(Q)$ is a structure factor ($S(0) = 1$ in the absence of interactions). Figure 6(a) shows an estimate of $S(Q)$ calculated via the Percus-Yevick approximation¹⁸ for particles of different polydispersities (σ_s) in the Schultz distribution of diameters D ($\sigma_s = 0$, for monodisperse particles). It may be seen that by a fortuitous combination of circumstances, excluded volume effects are manifested predominantly below the minimum Q of for an average diameter $\bar{D} \approx 1000$ Å. Moreover these effects are further damped by particle polydispersity and are virtually absent when the whole curve, as opposed to the small Q -region, is used in the analysis. Figure 6(b) shows experimental data compared to the core shell model latex (sample B) for the (PSH-co-PMMAH latex with PMMAD3 shell). Close examination of the curves for the Q -range $3 \times 10^{-3} < Q < 7 \times 10^{-3} \text{ Å}^{-1}$ illustrates that the experimental curve is slightly higher than the model, whereas for $7 \times 10^{-3} < Q < 9 \times 10^{-3} \text{ Å}^{-1}$ the data falls below the model. Comparison with Figure 6(a) indicates that such behavior is consistent with residual excluded volume effects. However, because of the indirect Fourier transform methods used, such effects do not perturb $d\Sigma(O)/d\Omega$, which agrees with the model prediction within the experimental error. Table I also shows the particle dimensions via SANS methods compared to those obtained by light scattering (LS) and electron microscopy (EM). The overall agreement is excellent. In view of the other uncertainties involved (absolute calibration, determination of the fraction of deuterated materials, slight mismatches in contrast match conditions, etc.), we believe that the core-shell model is a reasonable approximation for the scattering, both for the homopolymer³ and copolymer² latexes studied. Because of the extreme sensitivity of the scattering to the latex dimensions, it would only take a minor adjustment in the shell thickness to produce exact agreement with this model. For example, this could be achieved in the case of the SIA latex by changing the shell thickness for 31 to 24 Å, and this difference is probably within the overall experimental error.

Analysis of SANS data: II latexes polymerized by equilibrium swelling

The focus of this research was to produce latex particles in which the D- and H-labeled molecules are randomly distributed. When such latexes are suspended in an $\text{H}_2\text{O}/\text{D}_2\text{O}$ medium which matches the *average* SLD of the particle, the component of the scattering due to the latex spherical form factor vanishes, leaving only the scattering due to the D-labeled molecules within the latex. After correction for blank scattering and incoherent backgrounds the cross section is given¹⁰ by

$$\frac{d\Sigma}{d\Omega}(Q) = \phi x(1 - x)(a_H - a_D)^2 \frac{N_A \rho M_w}{(m_D)^2} S_s(Q) \quad (6)$$

where x is the fraction of molecules which are D-labeled ($x \approx 0.5$), a_H and a_D are the scattering lengths of H- and D-labeled monomer units, N_A is Avogadro's num-

ORNL-DWG 87-46409

ESTIMATION OF HARD-SPHERE EXCLUDED
VOLUME EFFECT IN CONCENTRATED ($\phi=0.4$)
SUSPENSIONS VIA PERCUS-YEVICK
APPROXIMATION (HAYTER, 1985)

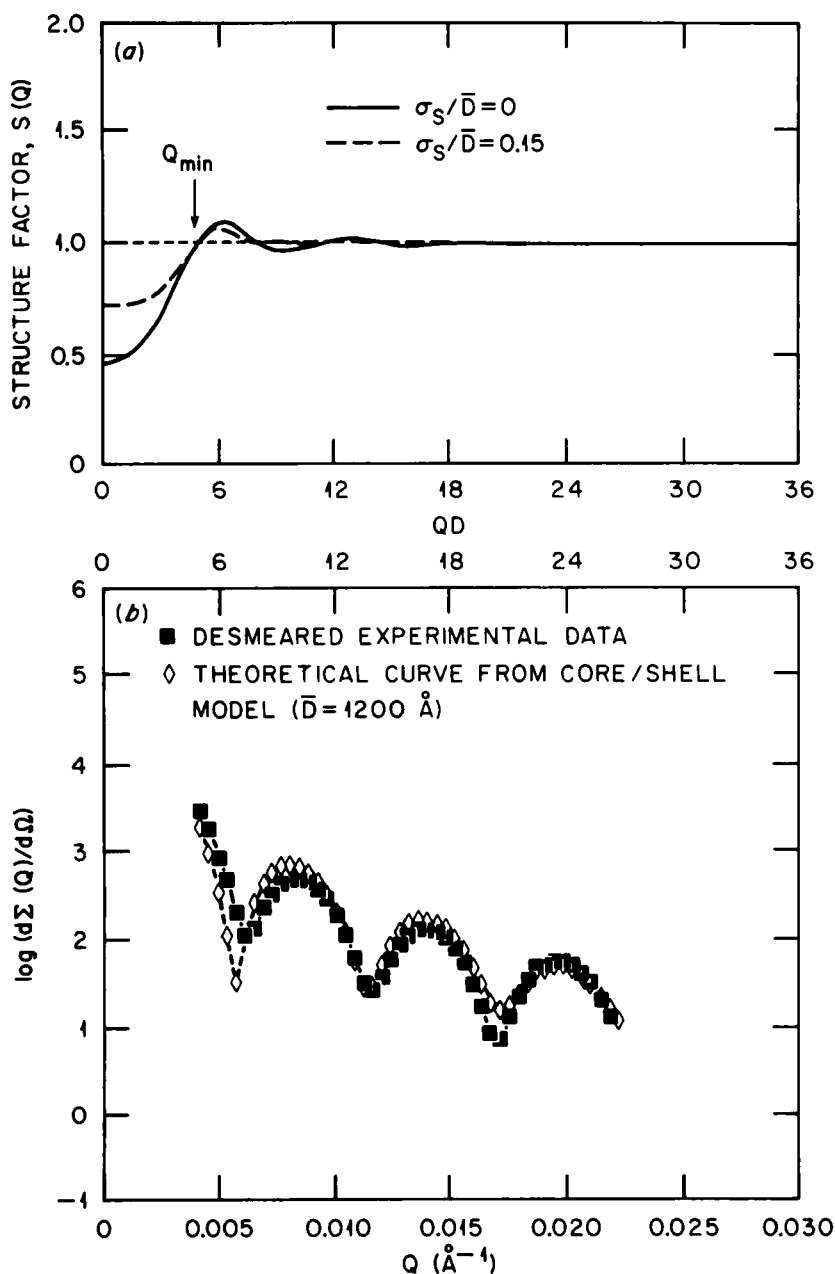


FIGURE 6

TABLE II
Sample (Weight-Averaged) Molecular Weight Characterization Via SANS and Gel Permeation Chromatography (GPC)

Sample No.	$M_w^{\text{GPC}} \cdot 10^{-6}$	$M_w^{\text{SANS}} \cdot 10^{-6}$	Ratio
25	0.0668	2.59	38.8
26	0.0783	13.6	174.1
27	0.0875	1.58	18.0
28	0.576	1.71	3.0
29	0.679	1.08	1.6
30	1.16	2.38	2.0
31	1.45	0.88	0.6
32	2.26	2.58	1.1
33	3.79	4.13	1.1

ber, ρ is the density of the latex and M_w and m_D are the molecular weight and monomer mass of a D-labeled chain. $S_s(Q)$ is the single chain form factor of the molecules ($S_s(Q) = 1$). The scattering arises only from the molecules within the latex particles which account for a fraction ϕ of the total sample volume. Similar methods have been used by Bates *et al.*,²³ to observe single block scattering within microphase separated domains in block copolymers. Equation 6 may be used to measure the SANS M_w of the labeled chains in the latex, which should equal the value measured by GPC. Typical molecular weight data are shown in Table II. For $M_w > 10^6$ the ratio of molecular weights measured by SANS and GPC is close to unity indicating that the labeled molecules are statistically distributed in the latex particles. Under these circumstances the measured weight-averaged radius of gyration, R_g^w , represents the single molecule and these values are shown in Table III for several different samples. Also shown are the end-to-end distances of the molecule constrained in the latex along with the value in relaxed state, i.e., in the bulk polymer. The molecules may be seen to be constrained from the relaxed state by factors $\sim 2 - 4$. To the authors' knowledge this represents the first determination of the constrained configuration in latexes. When such latexes are molded together into a film at temperatures above the glass transition temperature, the molecules will expand to the relaxed configuration. The time dependence of the scattering from such systems may be analyzed to explore interdiffusion and relaxation proc-

TABLE III
Dimensions of Polystyrene Molecules Constrained in Latex Particles

Sample No.	$M_w^{\text{SANS}} \cdot 10^{-6}$	R_g	Latex Diameter(Å)	End-to-End Distance (Å)	
				Constrained	Relaxed State
7	2.78	166	380	342	1123
8	5.85	178		368	1630
24	6.31	270	480	557	1693
33	4.13	231		477	1283
46	4.77	284	580	585	1475
55	4.21	288		594	1384

esses.^{24,25} Below $M_w \sim 10^6$ the SANS molecular weights systematically exceed the values measured by chromatography indicating that the labeled molecules are not statistically distributed in the latex. Several models were examined¹⁰ for this phenomenon, and it was concluded that the most probable cause of such behavior was the development of core-shell structures at lower molecular weights. Segregation in equilibrium swelled latexes depends on the ratio of the radius of gyration of the chain to the diameter of the particle. When the dimensions of the chain are approximately half that of the particle, segregation is at a maximum.¹⁰ At very low molecular weights, the shell is theorized to become infinitesimally thin. Such structures are presumably inhibited for very high molecular weights ($M_w > 10^6$) because of entropic considerations and the molecular intermixing caused by compressing large chains into a small volume. Intermixing does not apparently occur in the core-shell latexes studied^{2,3} because the polymerization conditions are different and also because the molecular weights of the components ($5 \times 10^4 < M_w < 2 \times 10^5$) are not sufficiently high for this mechanism to operate.

References

1. M. P. Grancio and D. J. Williams, *J. Polym. Sci. (A1)*, **8**, 2617 (1970).
2. M. P. Wai, R. A. Gelman, M. G. Fatica, R. H. Hoerl and G. D. Wignall, *Polymer*, **28**, 918 (1987).
3. L. W. Fisher, S. M. Melpolder, J. M. O'Reilly, V. R. Ramakrishnan and G. D. Wignall, *J. Colloid and Interface Sci.*, in press.
4. M. A. Linne, A. Klein and L. H. Sperling, *ANTEC Plastics*, **85**, 303 (1985).
5. J. W. Goodwin, *J. Colloid Interface Sci.*, **78**, 253 (1980).
6. L. W. Fisher, S. M. Melpolder, J. M. O'Reilly, V. R. Ramakrishnan and G. D. Wignall, presented at A.I. Ch.E., *Symposium on Polymer Colloids*, Houston, 1983.
7. J. M. O'Reilly, S. M. Melpolder and L. W. Fisher, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.*, **24**(2) (1983).
8. G. D. Wignall, *Trans. ACA*, **19**, 17 (1983).
9. G. D. Wignall, R. W. Hendricks, W. C. Koehler, J. S. Lin, M. P. Wai, E. L. Thomas and R. S. Stein, *Polymer*, **22**, 886 (1981).
10. M. A. Linne, A. Klein, L. H. Sperling and G. D. Wignall, *J. Macromol. Sci., Physics*, **B27**, 181 (1988).
11. I. Pirma, V. R. Kamath and M. Morton, *J. Polym. Sci., Polym. Chem. Ed.*, **3**, 2087 (1975).
12. W. C. Koehler, *Physica*, **137B**, 320 (1986).
13. G. D. Wignall and F. S. Bates, *J. Appl. Cryst.*, **20**, 28 (1987).
14. O. Glatter, *Acta Phys. Austriaca*, **47**, 83 (1977).
15. O. Glatter, in *Small-Angle X-ray Scattering*, ed. by O. Glatter and O. Kratky, Chapter 4, Academic Press, London, 1982.
16. P. B. Moore, *J. Appl. Cryst.*, **13**, 168 (1980).
17. V. Ramakrishnan, *J. Appl. Cryst.*, **18**, 42 (1985).
18. J. B. Hayter in V. Degiorgio and M. Corti, eds., *Proceedings of Enrico Fermi School of Physics Course XC*, Amsterdam (1985) p. 59.
19. J. B. Hayter and J. Penfold, *Colloid and Polymer Sci.*, **261**, 1022 (1983).
20. Lord Rayleigh, *Proc. R. Soc. Lond. A.*, **84**, 24 (1911).
21. R. Pecora and S. R. Aragon, *Chem. Phys. Lipids*, **13**, 1 (1974).
22. M. Kerker, *The Scattering of Light and Other Electromagnetic Radiation*, Academic Press, New York, 1969.
23. F. S. Bates, C. V. Berney, R. E. Cohen and G. D. Wignall, *Polymer*, **24**, 519 (1983).
24. J. E. Anderson and J. H. Jou, *Macromolecules*, **20**, 1544 (1987).
25. M. A. Linne, A. Klein, L. H. Sperling and G. D. Wignall, *J. Macromol. Sci., Physics*, **B27**, 217 (1988).