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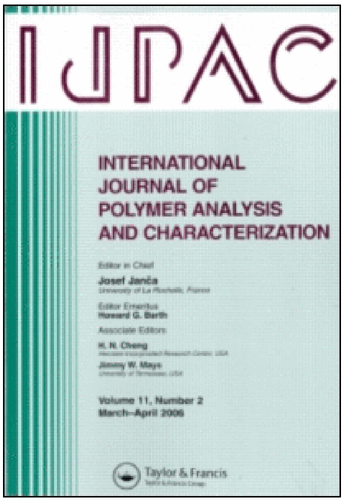

International Journal of Polymer Analysis and Characterization

Publication details, including instructions for authors and subscription information:
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To cite this Article Helmstedt, M. and Stejskal, J.(1998) 'Interpretation of Static Light Scattering Measurements by Two-Component Separation†', International Journal of Polymer Analysis and Characterization, 4: 3, 219 — 230
To link to this Article: DOI: 10.1080/10236669808009711
URL: http://dx.doi.org/10.1080/10236669808009711

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Int. J. Polym. Anal. Charact.,
1997 Vol. 4, pp. 219–230
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Interpretation of Static Light Scattering Measurements by Two-Component Separation[†]

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(Received 09 December 1996; In final form 30 May 1997)

Model calculations in combination with a two-component separation procedure allow a more advanced evaluation of static light scattering data in order to separate the contribution of macromolecules in polymer solutions and of the microgel or aggregates. As demonstrated by examples of polyethylene and gelatin, in this combination the well known physical models for scattering of spheres and linear and branched coils are successful in the interpretation of static light scattering data. The method is alaso applicable to polymer dispersions containing aggregated particles.

Keywords: Light scattering, molar mass determination, radius of gyration, hydrodynamic radius, polyethylene, gelatin, polymer dispersions

INTRODUCTION

The intensity of scattered light of polymer solutions or dispersions is proportional to the molar mass. That means, that even a small number of *relatively* big scatterers provides an important contribution to the intensity of scattered light. The presence of aggregated macromolecules, microgel particles or a small amount of dust along with polymer coils

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[†] Presented at the 9th International Symposium on Polymer Analysis and Characterization, Oxford, U.K., July 1–3, 1996.

may lead to incorrect weight-average molar or particle masses M_w and z-average radii of gyration $R_{G,z}$, although one can obtain exact averages of the 'mixture' in a physical sense. The interpretation of static light scattering measurement is of high interest for the characterization of polymers and some methods for correction and separation of light scattering intensity data were published.[1–22] The graphical Guinier approximation[13,14] has often been used. However, calculations using the fit of particle scattering functions, for example, for spheres according to Rayleigh[15] and Mie,[16] for linear coils by Debye,[17] for branched molecules by Dautzenberg *et al.*[18,19] or of Cassassa and Berry,[20] have been tried with success.

Wallenfels *et al.*[1] introduced the use of model scattering functions *in combination* with a two-component separation, a flexible concept used also by other groups. It allows a more advanced evaluation of static light scattering data in order to separate the contribution of single macromolecules in polymer solutions and of the large objects, microgels or aggregates. Results of our work with a slightly modified version of the method of Francuskiewicz and Dautzenberg[21] are presented in this paper. Later, Dautzenberg and Rother[22] introduced a master-curve procedure (including the calculation of logarithmic normal distribution of the parameters), which also can be used successfully in combination with the concept of two-component separation.

TWO-COMPONENT SEPARATION

The basic equations describing the two-component separation are

$$w_1 + w_2 = 1 \tag{1}$$

and

$$M_1^* + M_2^* = w_1 M_{w1} + w_2 M_{w2} = M_w = [(\mathrm{K}c / I_\Theta)_{c,\theta \to 0}]_{-1} \tag{2}$$

where w_i are the weight fractions and M_{wi} the molar masses of the main component ($i = 1$) and the second component ($i = 2$), c is the concentration, I_Θ is the Rayleigh ratio, and K is the 'contrast' factor of scattering for vertical polarized light of the wavelength λ_0,

$$\mathrm{K} = 4\pi^2 n_0^2 (\mathrm{d}n / \mathrm{d}c) / N_A \lambda_0^4 \tag{3}$$

where n_0 is the refractive index of the solvent, dn/dc is the refractive index increment of the polymer, and N_A the Avogadro number. M_i^* represent the apparent molar masses in the course of calculation.

We assume that the system under investigation can be approximated by a mixture of two components: Quasi-monodisperse (and in principle also polydisperse) single macromolecules represent the main component ($i = 1$). The second part is mainly represented by their assemblies, like microgels or aggregates ($i = 2$), which are assumed to be monodisperse, too, in order to simplify calculations. The intensity of the scattered light by both components is considered to be independent, which is justified for diluted systems. The intensities of both the components should be of the same order of magnitude. The procedure is illustrated in Figure 1: The experimental light-scattering envelope (values of Kc/I_Θ at angles Θ, typically extrapolated to $c = 0$), is fitted by particle scattering function for molar mass M_{w1} and radius of gyration R_{G1} of the majority component, $w_1 > 0.9$. In contrast to some of the other methods, the data are fitted by physical models for the scattering function of the macromolecules or particles: coils (linear or

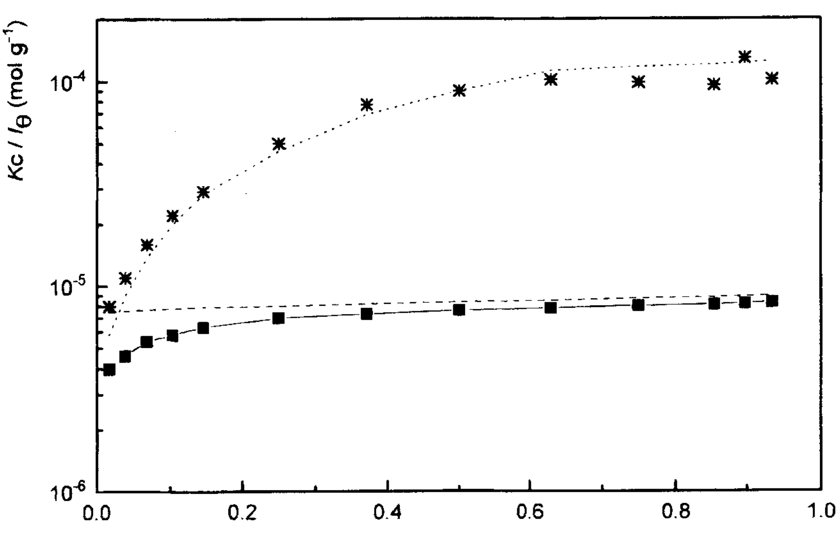

FIGURE 1 Scheme of the two-component separation of the angular dependence of scattered light, Kc/I_Θ. The values corresponds to experimental points (■), which were separated into contribution from individual macromolecules (dashed line); the difference (✳) was fitted by data for large structures of various nature.

branched), or spheres. As a second step, the *difference* of the result of model calculation and the experimental data is fitted by a scattering function for spherical scatterers or by using similar equations for branched macromolecules. Both can be successful for various types of dense particles like microgels.

In the course of the calculation, the *apparent* values M_1^* and M_2^* of molar mass are used. According to Equation (2), these are the products of weight fractions w_i and the *true* molar or particle masses M_{wi}. If w_2 is small, for example $w_2 < 0.01$, then $M_2^* = w_2M_{w2}$ is low in comparison with the particle size which is found by physical interpretation of the scattering envelope of the second component. The radii of gyration R_{Gi}, are also obtained by the calculation and (if we assume quasi-monodisperse components) they should approximately fulfill the additivity on a weight basis, too. In the case of polydisperse components, R_{Gi} are z-averaged. The true M_{wi} can be determined by using the $R_G - M_w$ relations which are known for the most polymers. The iterative calculation can be stopped when the conditions (1) and (2) are sufficiently satisfied by values of parameters w_i and M_{wi}. The reliability of the method was tested as follows: Gelatin was molecularly dissolved in aqueous 0.5M KSCN and measured by static light scattering as a model substance for the coil molecules. After addition of a very small amount of polystyrene dispersion with known particle diameter as a model for spherical scatterers, a remarkable change of the scattering envelope was observed. The separation procedure described here gave molecular weights and radii of gyration comparable with those for the individual components.[24] The method is illustrated by several examples described below.

EXPERIMENTAL

Fractions of branched polyethylenes were prepared by Brauer *et al.*[23] by elution fractionation. 1,2,4-Trichlorobenzene as a solvent for polyethylene was a product of Merck-Schuchardt, Germany. It contained 0.4 g/L phenyl-β-naphthylamine as an antioxidant. The polymer fractions were dissolved in ampoules at 150°C. The poly(methyl methacrylate) dispersions were prepared as described in refs.[24,27,28] *n*-Decane (purum, Fluka, Switzerland) was used as dispersion medium without further purification. The gelatin sample was produced by Gelatinewerke Calbe, Germany.

Static light scattering measurements were carried out with a SOFICA Photogoniodiffusometre Model 42000. The home-built version adapted for dynamic light scattering[24,29] and used for DLS measurements.

BRANCHED POLYETHYLENES

Diffusion and molecular parameters for fractions of branched polyethylenes were investigated in both good (tetralin, 1-chloronaphthalene and 1,2,4-trichlorobenzene) and theta (diphenylmethane) solvents by static and dynamic light scattering.[24] Here only the measurements in the good solvent, 1,2,4-trichlorobenzene, are discussed. The angular dependences of the inverse scattering intensity Kc/I_Θ, were separated into two *quasi-monodisperse* components, single macromolecules (i = 1) and 'random combs' (i = 2) of Casassa and Berry.[20] This model provides a good approximation for the size and mass of the branched macromolecules over a broad range of molar masses, including microgels. This example is used here as a representative of the other models available for branched polymers or other polymer architectures and particle shapes. The separation of components using the correlation functions measured by dynamic light scattering is done *independently* by Laplace inversion. This mathematical procedure, which is not described here, is based on a completely different mechanism.

The ratio of $\rho = R_G/R_H$ of the radius of gyration R_G, and the hydrodynamic radius R_H is a measure of the segment density of the branched macromolecules in solution. For the set of polyethylene fractions dissolved in good solvent, 1,2,4-trichlorobenzene, this ratio varied from 2.05 (for a fraction with low molar mass) down to 1.04 (for a fraction with very high molar mass) (Fig. 2), approaching slowly the theoretical value expected for hard spheres,[26] $\rho = 0.776$. This result supports the validity of two-component separation concept.

HIGHLY BRANCHED MACROMOLECULES

The random-comb model of Casassa and Berry[20] in combination with the two-component separation was reliable for solutions of low-density-polyethylene fractions in the usual range of molecular masses. For some

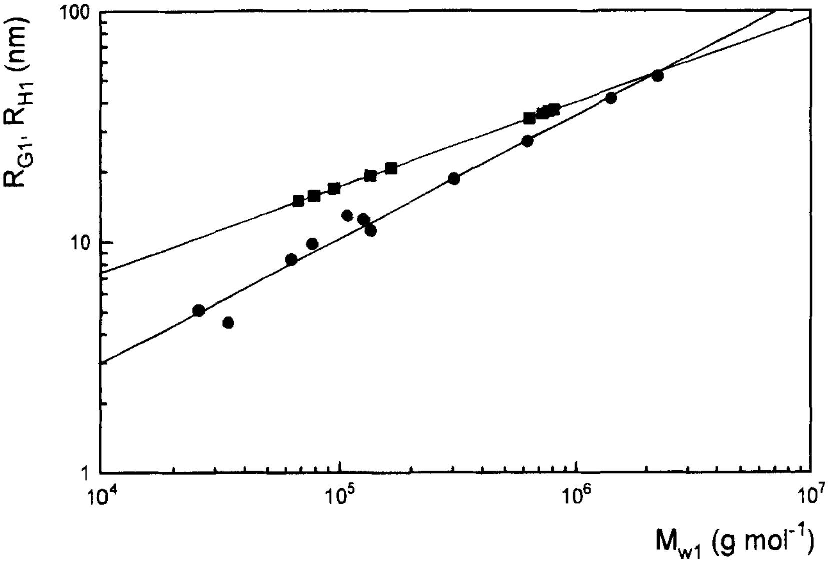

FIGURE 2 Radii of gyration R_{G1} (■) and hydrodynamic radii R_{H1} (●) of fractions of polyethylene (density 0.915 g cm^{-3}) as a function of the molar mass M_{w1} after two-component separation.

selected branched polyethylene fractions with extremely high molar mass, the specific scattering behavior of comb-like branched polymers was found (Fig. 3) *without* a two-component separation of the data. The curvature of the measured data at low angles cannot be fitted by other models as linear coils or spheres.

The data are fitted while assuming a relatively high density of long-chain branching: The long chain branching index is taken to be $\lambda_{LCB} \approx 2 \times 10^{-4}$ mol^{-1} and the fraction of segments in the side chains as $\beta_{LCB} = 30$–33% in accordance with other structural investigations.[23]

In light-scattering experiments, one cannot determine the intensity at small angles close to the primary beam. It is a main advantage of the described procedure, that this region is fitted by physical models, not by arbitrary straight or curved lines, and the extrapolation has a physical justification. The accuracy of the fit (and of the results!) especially in low-angle region, is increased and the determination of the molar mass is thus much more accurate.

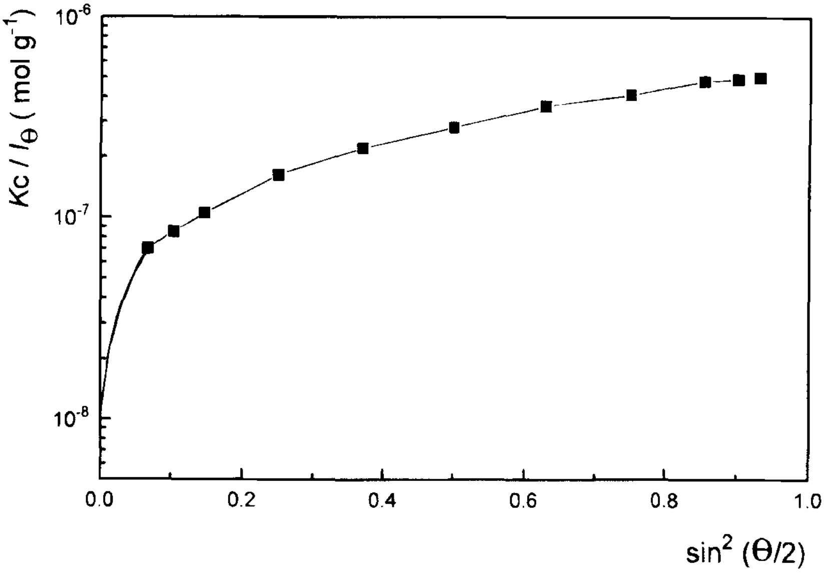

FIGURE 3 Angular dependence of Kc/I_Θ of a fraction of very high-molecular-weight polyethylene (■) and model calculation (line) with $M_w = 1.1 \times 10^8$ g mol^{-1} and $R_G = 252$ nm (weight fraction of the long-chain branched segments in the macromolecules $\beta_{LCB} = 0.3$ and the long-chain branching index $\lambda_{LCB} \approx 2 \times 10^{-4}$ mol g^{-1}).

GELATIN

In a similar manner one can separate single macromolecules ($i = 1$) and aggregated or gel particles of gelatin ($i = 2$), dissolved in aqueous solutions of potassium thiocyanate[25] (KSCN). Here, the formation of hydrogen bonds can be avoided and electrostatic interaction is screened by the presence of low-molecular-weight electrolyte. The scattering behavior of gelatin in water and in an aqueous potassium thiocyanate solution is shown in Figure 4. Whereas in electrolyte solutions it is typical of polymer coils accompanied by some crosslinked particles, in pure water the angular dependence of the intensity for spherical scatterers is unmistakable. This envelope approximately is fitted the scattering function of spheres with $R_G = 220$ nm and $M_w = 5 \times 10^7$ g mol^{-1}. It should be kept in mind that in this case the results may be affected by the polyelectrolyte effect because the measurement has been carried out in the absence of salt. More details and examples have been given elsewhere.[24]

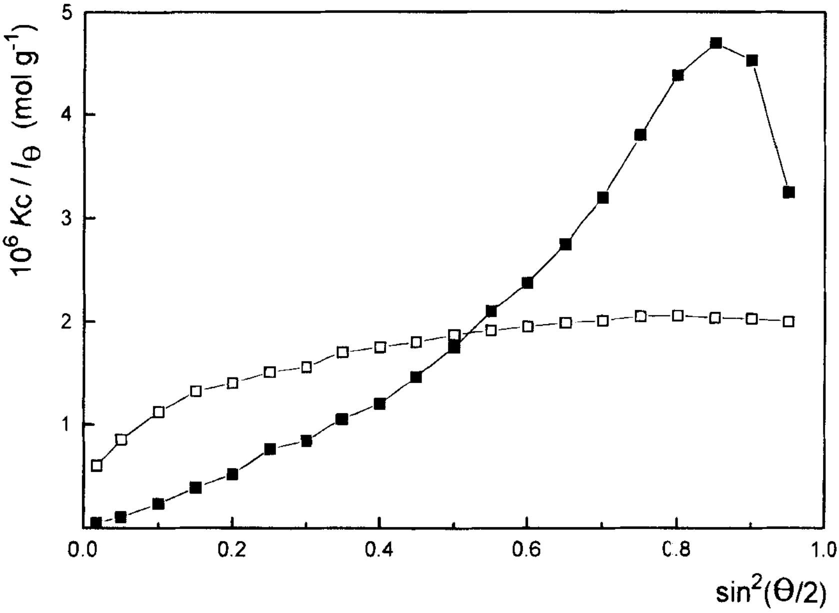

FIGURE 4 Angular dependence of scattered light, Kc/I_Θ, of gelatin dissolved in water (■, c = 1.00 g L^{-1}) and in 0.5 M aqueous KSCN (□, c = 1.91 g L^{-1}).

Typical results for the two-component separation of gelatin in electrolyte solutions are R_{G1} = 20–40 nm, M_{w1} = 2–6 × 10^5 g mol^{-1} for a molecularly dissolved component, and $R_{G2} \approx$ 200 nm and $M_{w2} \approx 10^8$ g mol^{-1} for a particulate component.

POLYMER DISPERSIONS

The procedure is also useful in the case of diluted polymer dispersions containing aggregated particles. For the determination of particle parameters of polymer dispersions, high dilution is needed and the stability of the diluted dispersions may be then limited. The presence of a small amount of aggregated particles is usually unavoidable. By uncritical evaluation of the Zimm plots, one may get biased results and the typical scattering behavior of spherical particles is distorted by the presence of aggregates.

The Zimm plot for a poly(methyl methacrylate) dispersion sterically stabilized by polystyrene-*block*-poly(ethylene-*co*-propylene) in *n*-decane is given in Figure 5. The standard evaluation of the data by common programs often yields results, that are not in agreement with the particle structure. The particle mass is found to be too high for a given radius, and the calculated density of particle core thus exceeds the density of poly(methyl methacrylate). The two-component separation and a fit by Rayleigh's formula for spherical scatterers[15] gave good results for the separation of single dispersion particles ($i = 1$) and their aggregates[27] ($i = 2$). The data for the second component are of no practical interest, because, in this case, the procedure has been used as a correction only. The radii of gyration, together with the hydrodynamic radii (Figure 6) from dynamic light scattering, allows the calculation of the ratio $\rho = R_{G1}/R_{H1}$, the densities of particle body and its shell (corona) of stabilizing copolymer, and consequently the exact description of the whole particle structure[24,27] is feasible. The ratio ρ is plotted in Figure 7 as a function of the fraction, x_I, of the aliphatic part of the stabilizing copolymer, poly(ethylene-*co*-propylene) block. The

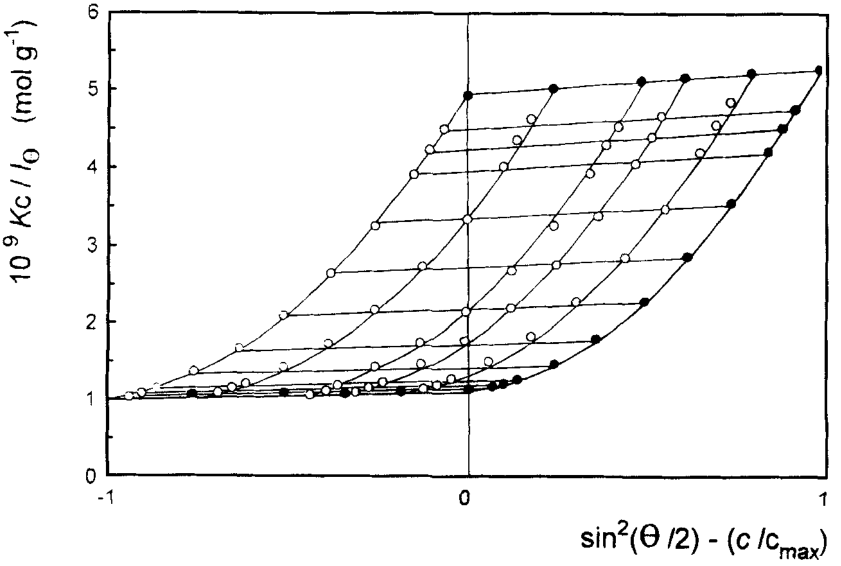

FIGURE 5 Zimm plot for a poly(methyl methacrylate) dispersion of particle mass $M_w = 1 \times 10^9$ g mol^{-1} in *n*-decane. The weight fraction of the stabilizing copolymer is x_s 0.029.

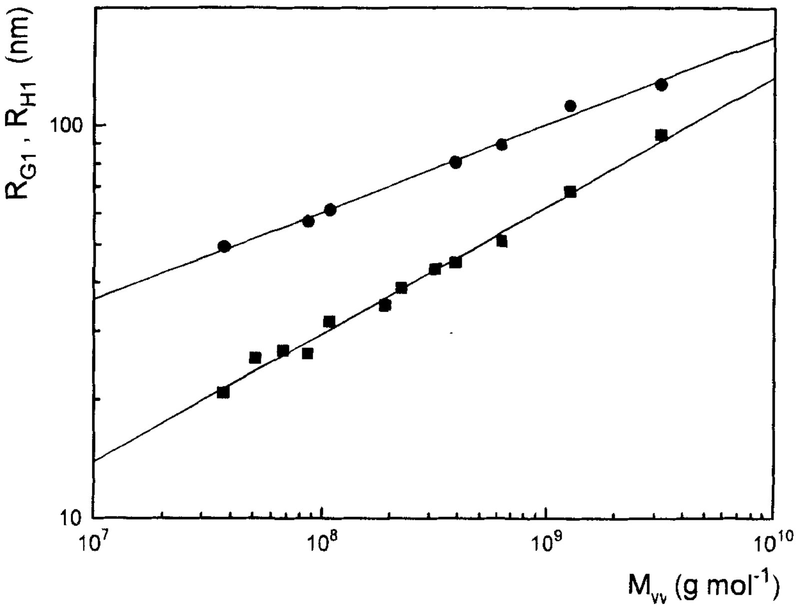

FIGURE 6 Radii of gyration R_{G1} (■) and hydrodynamic radii R_{H1} (●) of sterically stabilized poly(methyl methacrylate) dispersions as a function of the particle masses M_{w1} corrected by two-component separation.

ratio from the corrected data R_{G1} and R_{H1} at $x_1 = 0$ is approaching exactly $\rho = 0.776$, in agreement with the theoretical value for hard spheres,[26] whereas the ratio of uncorrected R_G and R_H values scatter strongly.

CONCLUSIONS

The two-component separation of light scattering intensities can provide additional insight into the evaluation of the experimental data and more detailed information on the system under study can be obtained. The use of this method is justified in cases when the nature of the system is known and can be approximated by two discrete components. Corrected data were obtained molar masses and sizes of macromolecules and microgels of branched polyethylenes and of gelatin, as well as for polymer dispersions. These would be incorrect under the standard treatment of the data because of partial aggregation of the particles. Size parameters can also be mea-

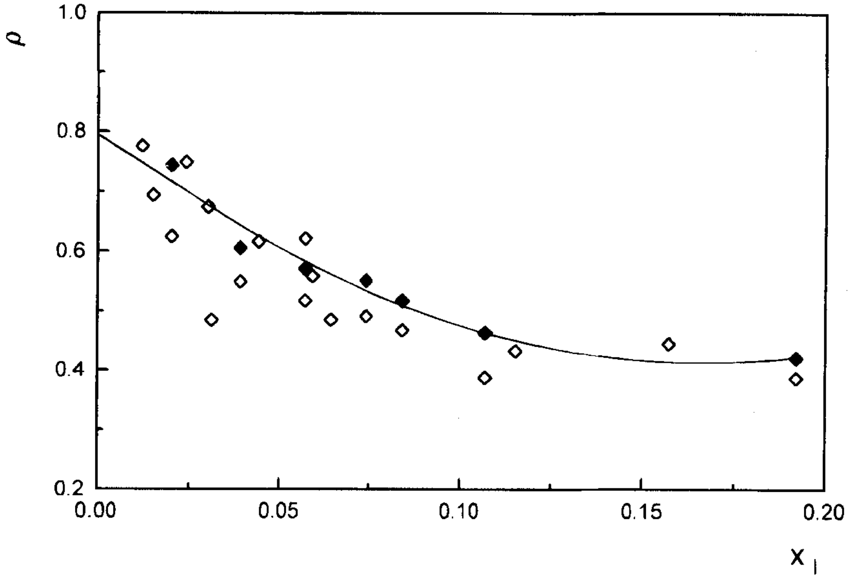

FIGURE 7 Ratio $\rho = R_G/R_H$ (◇) and $\rho = R_{GI}/R_{HI}$ (◆) as a function of the weight fraction x_I of poly(ethylene-*co*-propylene) stabilizer in poly(methyl methacrylate) dispersions in *n*-decane.

sured by other methods, namely by dynamic light scattering and Laplace inversion of the autocorrelation functions. One can combine the resulting parameters for both (practical) independent types of measurement and calculation.

Acknowledgements

The authors are indebted to the Deutsche Forschungsgemeinschaft (Projects He 2123/2-2 and 436 TSE 113/6) for the financial support.

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