

## Graft polymer solutions as sticky hard-sphere colloids

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We show that a solution of a graft (comb) polymer can exhibit an adhesive hard-sphere pair potential. In the present paper, static and dynamic light scattering measurements on a comb polymer at low molecular weight are performed and the results discussed in the framework of the colloidal theory for adhesive spheres. Renormalization group calculations are directly compared with experimental data on the cooperative diffusion coefficient using the scaled concentration parameter.

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### I. INTRODUCTION

Modifying the properties of synthetic macromolecules through the use of branching junctures has long been a challenging area of science and technology. Star polymers have had considerable impact on the field of materials science due to their unique mechanical, rheological, and solution properties, which depend on both the type and degree of branching [1,2]. The interest in studying star and starlike polymers, is based on the fact that they are inherently different from linear polymers of the same material, and it is this architectural difference that leads to many of the observed changes in their physical properties [3–5]. Because of this peculiarity they can be also employed, for example, as targeted drug delivery systems, in cell recognition, or for improving the therapeutic effect of many low molecular weight drugs.

In recent years, star polymers have been used as models (from both the theoretical and experimental points of view) for the study of the physics of complex fluids (for example, the prediction of the phase diagram [5] and the glass transition [3,4]). Moreover, graft copolymers with side chains that are chemically different from the backbone also have great relevance, because their properties can be modulated by the combination of selective interactions with solvents. This occurrence implies a high engineering potential [6].

The peculiarity of branched polymers, such as star polymers (and also graft and comb polymers) is that their physical properties can change to those of colloidlike systems on increasing the number of arms. Star polymers, for example, are well described by a soft (or ultrasoft) pair potential [3–5] constituted by a hard-sphere potential for stars with a high functionality (large number of arms) and by a repulsive potential (positive Yukawa for large distances and logarithmic behavior for short distances) for low functionality.

The main goal in the study of polymers consists in finding a direct correlation between the macromolecular chain structure and the macroscopic properties. The determination of polymer structural properties, therefore, turns out to be of paramount importance in an all-embracing interpretation of the structural and dynamical properties of these solutions. In particular, a better understanding of the interplay between the dynamics and the conformational properties is currently the

object of several studies which, beyond their academic interest, are fundamental for improving the employment and functionality of polymer materials in many technological fields.

The aim of this paper is to show that a solution of a graft polymer (comb polymer) can exhibit an adhesive hard-sphere pair potential. In particular solvents, a graft polymer constituted of two different polymers, one kind for the arms and another kind for the backbone, mimics a star polymer solution.

Here, static and dynamic light scattering measurements on a low molecular weight pPegma [7] comb polymer (polymer of polyethyleneglycol ethyl ether methacrylate) are performed and the results are discussed in the framework of the colloidal theory for adhesive spheres.

### II. GENERAL REMARKS

The static and dynamic properties of polymer solutions have often been studied in the framework of the virial expansion (static and dynamic) [8] and of the scaling theory [9] for dilute and semidilute solutions, respectively.

In the dilute regime, it is possible to evaluate the molecular weight  $M_w$ , the virial coefficient  $A_2$ , and the gyration radius  $R_G$  from static light scattering. The hydrodynamic radius  $R_H$  and the virial coefficient  $k_D$ , on the other hand, can be determined from dynamic light scattering. The static and dynamic behavior are related via the reduced interaction length  $x = S/R_H$ , where  $S$  is the equivalent hard-sphere radius used to represent the polymer interactions in solution:  $S = (3M_w^2 A_2 / 16\pi N_A)^{1/3}$  ( $N_A$  is the Avogadro number). The dynamic virial coefficient  $k_D$  has been calculated for many interaction potentials [10] as a function of  $x$ , giving useful information when compared with experimental data. Theoretical treatments predict different  $k_D$  behavior for different models describing the nature of the polymer-polymer interaction (e.g., for a hard sphere and for  $x=1$   $k_D=2$ ), ranging from theta to good solvent. The conformation of the polymer in solution can be estimated from the ratio [11]  $\rho = R_G/R_H$ ; for example, for well expanded coils  $\rho=1.8$ , for homogeneous spheres  $\rho=0.78$ , for rigid rods  $\rho>2$ , and for microgels [11,12] the  $\rho$  value is less than that of a homogeneous sphere (typically close to or below 0.5).

In the semidilute regime the entanglements of polymer chains cause a leveling off (and even a decrease) of the forward light scattering intensity. The concentration-normalized

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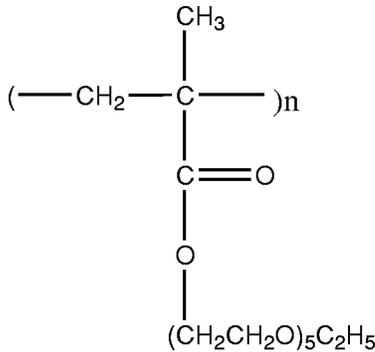


FIG. 1. pPegma structure.

inverse scattered intensity (proportional to the concentration derivative of the osmotic pressure  $\partial\Pi/\partial c$ ) shows a nonlinear behavior, generally obeying to a power law relation whose exponent is close to 5/4 [13]. At the same time, the cooperative diffusion coefficient does not follow a linear behavior (the virial regime under dilute conditions) and obeys a power scaling law whose exponent is close to 3/4 [9].

The concentration  $c^*$ , that defines the crossover between the dilute and semidilute regimes, is written as  $c^* = 3M_w/(4\pi N_A R^3)$ , where  $R$  is generally assumed to be equal to  $R_G$ . The experimental crossover value can differ from  $c^*$  by even a factor of 5. The intuitive definition of  $c^*$  is the concentration value at which polymer chains overlap and entanglements become significant.

Renormalization group (RG) calculations [14,15] have been successful in understanding the dynamical quantities of these polymer solutions. This theory predicts the behavior of the ratio between the effective hydrodynamic radius and the hydrodynamic radius in the dilute limit, in the whole range of concentration, as a function of the reduced concentration  $X$ . The latter is an overlap parameter defined as  $X = 2cM_w A_2 / \{1 + \exp[1/4(1 + \ln 2)]\}$  [14] or as  $16/9 A_2 M_w c$  [16] or more simply as  $A_2 M_w c$  [9,11]. In practice, however, the best agreement between the RG theory and the experimental results is obtained by using the experimental value  $X = k_D^c c$  (in this last assignment the dynamical virial coefficient  $k_D^c$  is used instead of the static one  $A_2$ ) [17,18].

### III. SAMPLES AND DATA ANALYSIS

The polymer matrix pPegma, shown in Fig. 1, is constituted of polyethyleneoxide (PEO) arms (five monomers) grafted to a methacrylate backbone. We used ethanol as solvent, in which the polyethyleneoxide arms are well swollen in comparison with the methacrylate backbone. The concentration range investigated varies from  $c = 7.9 \times 10^{-5}$  to  $0.17 \text{ g/cm}^3$  at a constant temperature value of  $25^\circ\text{C}$ .

In order to obtain information on the relevant parameters involved in the interaction potential and in the conformation of polymer chains, static and dynamic light scattering experiments were carried out. A brief review of the quantities measured in these experiments is reported in the following.

The absolute excess scattered intensity  $R_R$  from a volume  $V$  of the system at a distance  $R$ , when illuminated with monochromatic linearly polarized light  $I_0$ , is

$$R_R(k) = \frac{I_s(k)}{I_0} \frac{R^2}{2V \sin^2 \gamma} = KM_w c P(k) S(k), \quad (1)$$

where  $I_s$  is the scattered intensity,  $P(k)$  and  $S(k)$  the normalized form factor and the structure factor, respectively,  $\gamma$  the angle between the polarization of the incident light and the scattering plane, and  $K$  the optical constant defined as [19]

$$K = \frac{2\pi n^2}{\lambda_0^4 N_A} \left( \frac{dn}{dc} \right)^2. \quad (2)$$

The exchanged wave vector  $k$  is related to the scattering angle by  $|k| = (4\pi n/\lambda) \sin(\theta/2)$ , where  $n$  is the refractive index of the solvent and  $\lambda_0$  the wavelength of light in vacuum. The field autocorrelation function [20]

$$G_1(k, t) = \langle E^*(k, t_1) E(k, t_1 + t) \rangle \quad (3)$$

[for which  $G_1(k, 0) = I_s(k)$ ] for Gaussian scatterers is related to the measured intensity autocorrelation function  $G_2(k, t)$  by

$$G_2(k, t_1, t_2) = I_s(k)^2 [1 + |G_1(k, t_1, t_2)|^2], \quad (4)$$

and its logarithmic derivative (or, more generally, its cumulant expansion) gives the cooperative diffusion coefficient  $D_c$ .

We used a homemade computer controlled goniometric light scattering apparatus [21] with a duplicate neodymium-doped yttrium aluminum garnet (Nd:YAG) (532 nm) laser at a power of 200 mW. The laser beam is linearly polarized orthogonally to the scattering plane. The angular range explored is  $20^\circ$  to  $150^\circ$ . For the correlation function measurements we used a BIC (Brookhaven Instrument Corp.) correlator in a homodyne (self-beating) detection mode, in the delay range 25 ns to 1 s. In order to minimize correlation of the photomultiplier afterpulse we used two photomultipliers (at the same scattering angle) in cross configuration. For all the samples investigated the correlation function  $G_1(t)$  shows a single relaxation mode (a second relaxation slow mode with a small amplitude starts to appear at higher concentration values) [22].

### IV. RESULTS AND DISCUSSION

In the whole concentration range investigated the scattered intensity and the cooperative diffusion coefficient are  $k$  independent; therefore, in the following we shall omit the exchanged wave vector label  $k$  and set  $P(k) = 1$ .

The average molecular weight  $M_w$  and the static second virial coefficient  $A_2$  were calculated using the low concentration expansion of  $S(0)^{-1} = 1 + 2A_2 M_w c$ , which gives

$$cK/R_R = (1/M_w)(1 + 2A_2 M_w c). \quad (5)$$

In Fig. 2 the excess elastic light scattering intensity at  $90^\circ$  scattering angle is reported as a function of concentration  $c$ . In the inset a plot of the scaled inverse excess scattering intensity is also reported. From the extrapolation at zero concentration we obtain the inverse of the average molecular

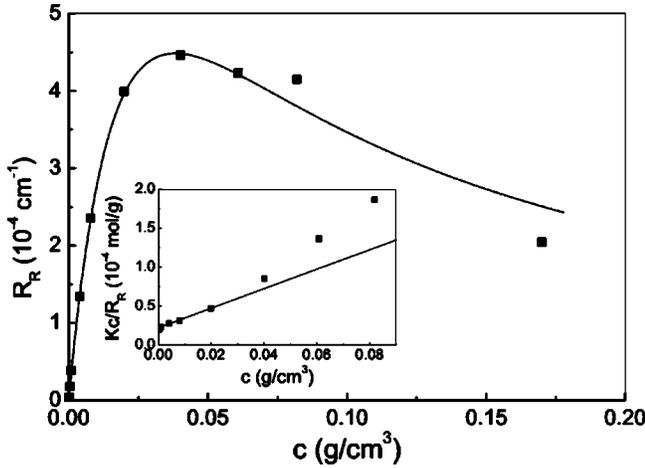


FIG. 2. Excess scattered intensity as a function of concentration. The continuous curve is the fit result using Baxter's adhesive hard-sphere model. In the inset the normalized inverse excess scattered intensity is reported; the straight line is the fit according to the virial expansion theory.

weight; in this way  $M_w = 45\,000 \pm 2000$  can be determined, and from the initial slope we extract the second virial coefficient  $A_2 = (5.3 \pm 0.5) \times 10^{-4} \text{ cm}^3 \text{ mol/g}^2$ . Similar results are obtained by using Berry's plot [23].

If the equivalent hard-sphere radius  $S = (3M_w^2 A_2 / 16\pi N_A)^{1/3}$  ( $S \approx 5 \text{ nm}$ ) is used for the calculation of  $c^* = 3M_w / (4\pi N_A S^3)$ , we obtain  $c^* = 4 / (M_w A_2) \approx 0.17 \text{ g/cm}^3$ , which is the contact concentration of spheres having radius  $S$  and mass  $M_w$ . From the latter quantity the average number of arms is estimated to be close to 135 (this is calculated by dividing the molecular weight of the polymer by that of a single monomer, whose grafted chain is made up by five monomers of ethyleneoxide) and is equal to the polymerization degree of the pPegma.

For interpretation of the excess scattering intensity in the whole range of concentration we need a model for the concentration dependence of  $S(0)$ . The large number of arms suggests that the asymptotic hard-sphere behavior of star polymers might be valid [24]. But the simple hard-sphere solution of the Ornstein-Zernike equation [25] for  $S(0)$ , applied to our experimental data, furnishes an inconsistent value for the ratio  $c/\phi$  (where  $\phi$  is the volume fraction of the colloidal particles in the system); in fact, the best fit gives a value of  $c/\phi$  greater than  $2c^*$  (and thus a too small sphere radius). In order to see the effect of a repulsive potential added to the hard-sphere model, we added a positive quadratic term in  $\phi$  to the osmotic pressure and calculated the relative  $S(0)$  [26]. This perturbative repulsion added to the hard-sphere potential did not remove the inconsistency. This occurrence suggested taking into account intermolecular attractive interactions together with the excluded volume interactions (hard sphere). With this approach we have consistent results. If one regards the backbone core of the polymer as a solvent-impenetrable sphere with several (but short) grafted swollen arms (see Fig. 3), the physical origin of these attractive interactions can be attributed both to the depletion of the solvent because of the interpenetration of the arms and to the

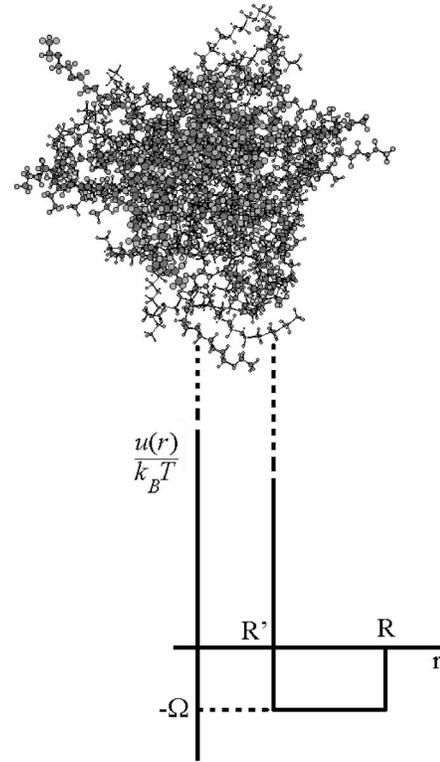


FIG. 3. Molecular mechanics representation of the pPEGMA conformation [performed using the CHEMOFFICE energy minimization (MM2) for a number of arms equal to 48] and sketch of the interparticle potential (see text for details).

interaction between PEO arms. In fact, ethanol is not as good a solvent as water for PEO, thus giving rise to polymer-polymer interactions which are competitive with the polymer-solvent interaction contribution.

In order to take into account this attraction, we used Baxter's adhesive hard-sphere model [27,28], which describes the potential  $u(r)$  for a sphere of radius  $R$  as

$$\frac{u(r)}{k_B T} = \begin{cases} \infty & \text{for } 0 < r < R' \\ -\Omega & \text{for } R' < r < R \\ 0 & \text{for } R < r, \end{cases} \quad (6)$$

where  $R - R'$  is the thickness of the adhesive layer,  $\Omega$  the adhesive potential, and  $k_B T$  the thermal energy. Baxter solved the Ornstein-Zernike equation [25] in the Percus-Yevik approximation [29] in the limit where the thickness approaches zero but the stickiness parameter  $1/\tau$ , defined as  $1/\tau = 12 \exp(\Omega)(R - R')/R$ , remains finite. This limit is called the sticking sphere model, and the resulting structure factor is an analytical function of the volume fraction  $\phi$  (or sphere radius) and of the sticking parameter  $1/\tau$ . The structure factor at zero exchanged wave vector, expanded in powers of the volume fraction, is [30]

$$\frac{1}{S(0)} = 1 + \left(8 - \frac{2}{\tau}\right)\phi + \frac{18\tau + 192\tau^3 - 90\tau^2 - 1}{6\tau^3}\phi^2 + \dots \quad (7)$$

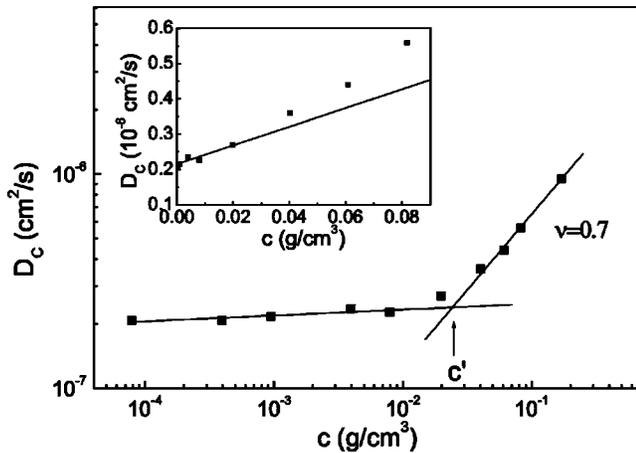


FIG. 4. Dependence of the collective diffusion coefficient as a function of concentration. The two straight lines allow for the identification of the experimental overlap concentration  $c'$ ; the slope of the line in the semidilute regime is the exponent of the power law  $D_c \propto c^\nu$  (see text for details). The inset shows only the dilute regime and the straight line is the result of the fit according to the dynamic virial expansion.

In Fig. 2, we report the best fit of Eq. (1) with  $S(0)$  given by Baxter's expansion [Eq. (7)]. From the fit parameters we obtained  $1/\tau = 0.7 \pm 0.2$ ,  $M_w = 45\,000 \pm 2000$  (the same value as that obtained from the virial expansion), and  $c/\phi = 0.18 \pm 0.01$  g/cm<sup>3</sup> (in good agreement with  $c^*$  calculated from the virial expansion). Moreover, the corresponding sphere radius  $R \approx 5$  nm is in agreement with  $S$ .

The behavior of  $D_c$  for low concentration [ $D_c = D_0(1 + k_D^c c)$ ,  $D_0$  being the diffusion coefficient at infinite dilution], reported in the inset of Fig. 4, furnishes the hydrodynamic radius of the polymer,  $R_H = 8.5 \pm 0.5$  nm, from  $D_0 = (k_B T / 6\pi \eta R_H)$ , and the virial dynamic coefficient  $k_D^c = 12 \pm 2$  cm<sup>3</sup>/g ( $\eta$  is the viscosity of the solvent). The corresponding dynamic coefficient is  $k_D^0 = k_D^c c^* \approx 2$ , in agreement with that measured in hard-sphere systems, but with an unusually low  $x$  value.

In order to prove that this value of the hydrodynamic radius refers to a single chain (so excluding the presence of micellar aggregates), we performed dynamic light scattering using acetonitrile as solvent in the low concentration region (below  $c = 0.02$  g/cm<sup>3</sup>). Acetonitrile is a good solvent for both backbone and side groups and it should be able to avoid micelle formation. From the extrapolation to infinite dilution of the collective diffusion coefficient we found a hydrodynamic radius equal to  $10 \pm 0.5$  nm. This result indicates that in both ethanol and acetonitrile single polymer chains (not aggregated chains) are present. The hydrodynamic radius is slightly larger than that in ethanol because in ethanol the single polymer entities take a starlike conformation, in which the methacrylate backbone is confined in the inner part (where ethanol does not penetrate) by the PEO side chains, whereas in the other case acetonitrile penetrates more uniformly into the chain, which takes a swollen conformation.

Coming back to the polymer in ethanol, for more concentrated solutions ( $0.04 < c < 0.17$  g/cm<sup>3</sup>) (see Fig. 4), the power law  $D_c \propto c^\nu$  is observed, with  $\nu = 0.7 \pm 0.05$ . Although

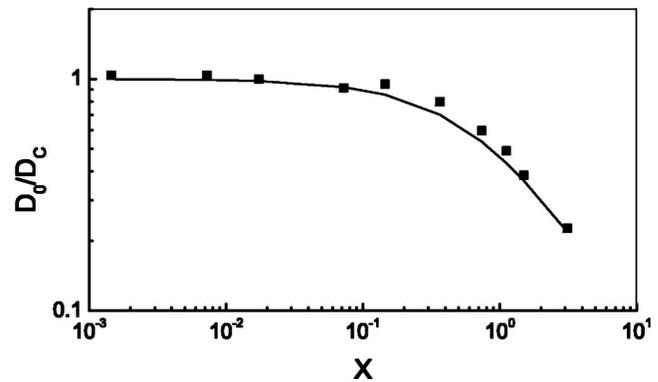


FIG. 5.  $D_0/D_c$  behavior as a function of the reduced parameter  $X$ . The continuous curve is the theoretical master curve resulting from the RG calculations.

this value differs from the theoretical one ( $\nu = 0.75$ ) predicted by de Gennes [9], it agrees with that observed in other systems [31].

The experimental crossover concentration value  $c'$  is lower than  $c^*$ , but close to  $3M_w / (4\pi N_A R_H^3)$ , namely, the value at which spheres of radius  $R_H$  come into contact. This concentration value marks the onset of the semidilute regime for the dynamics. The dynamic behavior in the whole concentration range is described using the renormalization group calculation in which the reduced concentration  $X$  is exploited.

The renormalization group theory for polymer solutions predicts the behavior of the cooperative diffusion coefficient  $D_c$  in a three-dimensional system, in the absence of hydrodynamic screening in the whole concentration range as [14]

$$\frac{D_0}{D_c} = \frac{(1+X)^{3/8}}{1 + (1+X)^{1/4} X \exp[(1/4)(1 + \ln 2)]}, \quad (8)$$

where  $X = 2cM_w A_2 / \{1 + \exp[(1/4)(1 + \ln 2)]\}$  is the overlap parameter (reduced concentration variable).  $D_0/D_c$  is the ratio between the effective and the hydrodynamic radii extrapolated at zero concentration. In Fig. 5, we report the experimental  $D_0/D_c$  and the corresponding values obtained from Eq. (8) (continuous line) as a function of  $X$ . As can be seen, they are in good agreement with one another.

## V. CONCLUDING REMARKS

In summary, we have shown that polymer solutions can be modeled as sticky hard-sphere colloids. In particular, pPegma/ethanol solutions have a stick parameter  $1/\tau = 0.7$  and exhibit microgel structures evidenced by the low value of  $\rho$ .

In fact, from the static and dynamic light scattering measurements we can conclude that both the values of the reduced interaction length  $x = S/R_H \approx 0.5$  and of the ratio  $\rho = R_G/R_H = (3/5)^{1/2} S/R_H \approx 0.4$  support the picture that the polymer is constituted of local microgel structures rather than of hard spheres or random coils.

The renormalization group calculations were directly compared with the experimental data of the cooperative dif-

fusion coefficient using the scaled concentration parameter  $X$  as in Ref. [14], in which the static virial coefficient  $A_2$  is involved. We would like to note also that using the overlap parameter, defined as  $X = k_D^c c$ , leads to an analogously good result.

We would like to remark that this particular star polymer has an unusual interaction potential. In fact, to our knowledge, Baxter's model has never been used for describing

intermolecular interactions in star polymers. For these systems the model used up to now is that of soft or ultrasoft spheres (always repulsive).

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