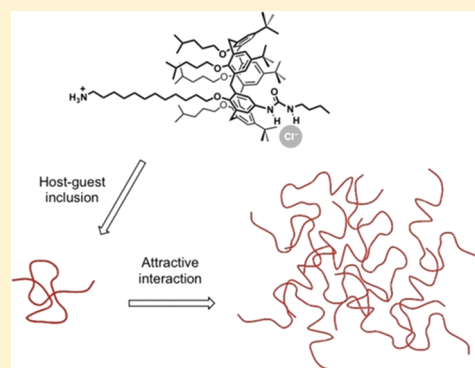


## Self-Assembled Calixarene Derivative as a Supramolecular Polymer

Valentina Villari,<sup>\*,†</sup> Giuseppe Gattuso,<sup>‡</sup> Anna Notti,<sup>‡</sup> Andrea Pappalardo,<sup>§</sup> and Norberto Micali<sup>†</sup><sup>†</sup>CNR-IPCF Istituto per i Processi Chimico-Fisici, Viale F. Stagno d'Alcontres 37, 98158 Messina, Italy<sup>‡</sup>Dipartimento di Chimica Organica e Biologica, Università di Messina, Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy<sup>§</sup>Dipartimento di Scienze Chimiche, Università di Catania, Viale Andrea Doria 6, 95125 Catania, Italy

## S Supporting Information

**ABSTRACT:** A light scattering study shows that the HCl-promoted self-assembly of an amino-calix[5]arene monomer precursor **UC5-NH<sub>2</sub>**, bearing an ancillary ureido binding site, efficiently yields supramolecular polymers with a concentration-independent average mass. These polymers adopt a random-coil conformation and interact among themselves via the adhesive hard sphere pair potential. The findings also indicate the formation of polymer clusters, coexisting in low concentration with the polymers and resulting from the adhesive interpolymer interactions. Unlike polymers, the size of these clusters depends on the monomer concentration.



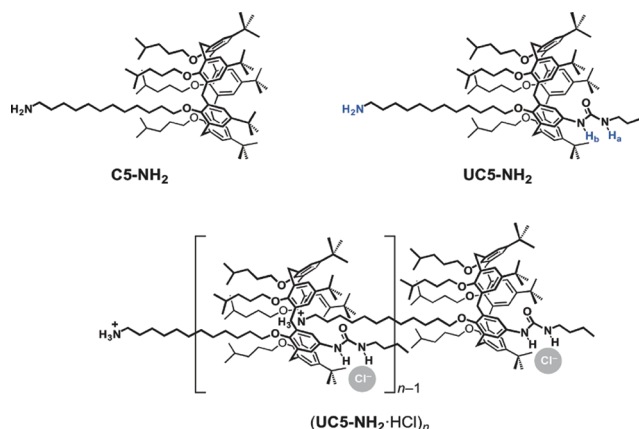
## ■ INTRODUCTION

In recent years, a great deal of effort has been devoted to the construction of supramolecular polymers,<sup>1–3</sup> by taking advantage of different types of specific noncovalent interactions (e.g., hydrogen bonding,  $\pi$ – $\pi$  stacking, metal coordination).<sup>4–6</sup> Less common, but increasingly more popular, are polymeric systems based on host–guest interactions (for some recent examples, see refs 7–11). Calixarenes, for instance, have been shown to be efficient building-blocks for the assembly of such supramolecular species.<sup>12–15</sup> Supramolecular polymer formation, being driven by reversible noncovalent interactions, is generally found to be a concentration-dependent process and, consequently, the degree of polymerization keeps on growing upon increasing the monomer concentration. As a result of this, characterization of the polymers formed and assessment of the interaction potential among them is very often prevented. Some authors<sup>16</sup> have recently qualitatively pointed out how crucial the role played by attractive and repulsive interactions among monomers is for obtaining structures with well-defined size and low polydispersity, but determination and modeling of the pair interaction potential has not yet received much attention.

Previously, we have investigated a pH-responsive amino-dodecyloxy-calix[5]arene derivative (**C5-NH<sub>2</sub>**) that, upon contact with a variety of acids, reversibly self-assembles into linear oligomers as a result of an intermolecular iterative host–guest inclusion process.<sup>17</sup> However, owing to the intrinsically saline nature of the monomers used, the growth of these aggregates was found to depend on the strength of the ion-pairing effect between the ammonium monomer (formed upon acid treatment) and its counterion. In the course of subsequent studies, to facilitate the acid-promoted head-to-tail self-assembly of this monomer, we have covalently added an

ancillary anion-binding site (i.e., an ureido moiety<sup>18–22</sup>) at its upper rim (**UC5-NH<sub>2</sub>**; see Scheme 1).<sup>23</sup>

Scheme 1



Herein, by a light scattering investigation, we demonstrate that the HCl-promoted supramolecular polymerization of **UC5-NH<sub>2</sub>** in  $\text{CH}_2\text{Cl}_2$  yields polymers that, once formed, are nearly monodisperse and have a concentration-independent average degree of polymerization in the whole concentration range explored. The present study sheds light on the polymer chain conformation and on the interpolymer interaction

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potential, whose role is of paramount importance for the stability of supramolecular polymers.

## EXPERIMENTAL SECTION

**Materials.** A solution of the amino-calix[5]arene monomer precursor UC5-NH<sub>2</sub> (100 mg in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>) was gently shaken with 10 mL of an aqueous HCl solution (1 M). The organic layer was separated, washed twice with 5 mL of H<sub>2</sub>O, dried (MgSO<sub>4</sub>), and concentrated to dryness under reduced pressure. The solid residue thus obtained was kept under vacuum (1 h, at room temperature) and used as such to prepare the relevant CH<sub>2</sub>Cl<sub>2</sub> solutions, which were filtered through a PTFE filter (0.20 μm pore size) prior to analysis.

**Method.** Light scattering experiments<sup>24</sup> were performed by using a He–Ne laser source (λ<sub>0</sub> = 632.8 nm) at a power of 10 mW, linearly polarized orthogonally to the scattering plane, and a homemade computer controlled goniometric apparatus that collected the scattered light in a pseudocross correlation mode (through two cooled R942-02 photomultipliers at the same scattering angle). The temperature was controlled by a homemade water-circulating apparatus at 25 ± 0.01 °C.

The scattered light, collected in a self-beating mode, was analyzed by a MALVERN 4700 correlator to build up the normalized intensity autocorrelation function,  $g_2(Q, t) = \langle I(Q, 0)I(Q, t) \rangle / \langle I(Q) \rangle^2$ ,<sup>25,26</sup> where  $|Q| = (4\pi n / \lambda_0) \sin(\theta/2)$  (θ being the scattering angle, *n* the refractive index of the solution, and λ<sub>0</sub> the wavelength of light in vacuum). For scattered electric fields obeying Gaussian statistics, the Siegert's relation holds:

$$g_2(Q, t) = 1 + \alpha |g_1(Q, t)|^2 \quad (1)$$

where α is a constant depending on the experimental setup, and  $g_1(Q, t) = \langle E_s^*(Q, 0)E_s(Q, t) \rangle / \langle I(Q) \rangle$  is the normalized scattered electric field autocorrelation function.

For diffusing monodisperse spherical scatterers with radius *R*, the normalized field autocorrelation function takes a simple exponential form,  $g_1(Q, t) = \exp(-\Gamma t)$ . Under the condition  $QR \ll 1$ , Γ is related to the collective diffusion coefficient, *D<sub>c</sub>*, by the relation  $\Gamma = D_c Q^2$ . However, if the diffusing spherical scatterer is rigid, the latter relation is fulfilled also for  $QR > 1$ .

At infinite dilution, the Einstein–Stokes relation,  $R_H = k_B T / (6\pi\eta D_0)$ , can be used to obtain the hydrodynamic radius *R<sub>H</sub>* of the scatterers from their diffusion coefficient, *D<sub>0</sub>* (*k<sub>B</sub>* being the Boltzmann's constant, *T* the absolute temperature, and η the solvent viscosity).

At finite concentration, in the dilute regime, the generalized Einstein–Stokes relation gives (in the  $Q \rightarrow 0$  limit) the concentration dependence of the collective diffusion coefficient, *D<sub>c</sub>*:<sup>26</sup>

$$D_c = D_0(1 + k_D c) \quad (2)$$

*k<sub>D</sub>* being the dynamic virial coefficient.

For static light scattering measurements, the scattered intensity of the solvent is subtracted from that of the solutions; then, the obtained angular profile is normalized by the scattered intensity of toluene, used as a reference. The normalized scattered intensity can be written as<sup>25–27</sup>

$$I(Q) = K M_w c P(Q) S(Q) \quad (3)$$

*P(Q)* and *S(Q)* being the normalized form factor and structure factor respectively, *M<sub>w</sub>* the weight-average molecular weight of the particle, *c* the mass concentration, and  $K = 4\pi^2 n^2 (dn/dc)^2 / (\lambda_0^4 N_A)$  the optical constant<sup>27</sup> (with *N<sub>A</sub>* the Avogadro's

number). The *dn/dc* value is 0.11, as measured by using a differential refractometer.

Owing to the  $Q \rightarrow 0$  limit typical of light scattering, for small particles (for which  $P(Q) = 1$ ), the structure factor does not depend on *Q* and can be approximated to  $S(Q = 0)$ , for which the virial expansion for the osmotic compressibility valid at low concentration is

$$S(0) = \frac{1}{[1 + 2A_2 M_w c]} \quad (4)$$

*A<sub>2</sub>* being the static virial coefficient.

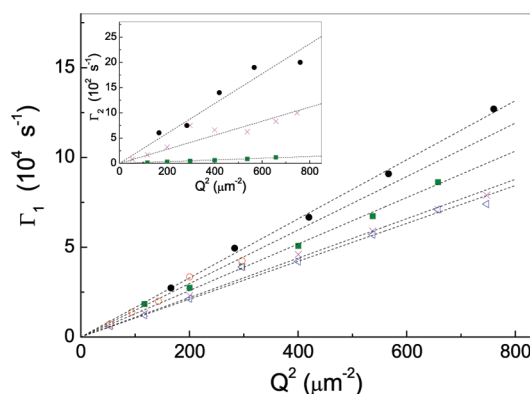
From the generalized Einstein–Stokes equation, it turns out that  $k_D = k_1 - k_f$ , where  $k_1 = 2A_2 M_w$  and *k<sub>f</sub>* is the second virial coefficient of the friction interactions.<sup>26</sup>

## RESULTS AND DISCUSSION

Dynamic light scattering measurements show that the scattered electric field autocorrelation functions are composed of two distinct relaxation processes, well represented by two exponential decays:

$$g_1(t) = a_p \exp[-\Gamma_1 t] + a_c \exp[-\Gamma_2 t] \quad (5)$$

Both the fast, Γ<sub>1</sub>, and the slow, Γ<sub>2</sub>, relaxation rates are *Q*<sup>2</sup>-dependent in the whole concentration range investigated, thus indicating the diffusive nature of the detected decays (see Figure 1). The fast mode can be related to the collective



**Figure 1.** Fast decay rate of the correlation function as a function of the squared wave vector at different concentration values:  $7.1 \times 10^{-3}$  g/cm<sup>3</sup> (full circles),  $1.4 \times 10^{-2}$  g/cm<sup>3</sup> (open circles),  $5.6 \times 10^{-2}$  g/cm<sup>3</sup> (triangles),  $8.4 \times 10^{-2}$  g/cm<sup>3</sup> (crosses), and 0.12 g/cm<sup>3</sup> (squares). In the inset, the slow decay rate is reported for some concentrations as an example. The dashed lines indicate linear fits.

diffusion of polymers, whereas the slow one is related to that of clusters of polymers. The goodness of the fit with an exponential decay indicates that the polydispersity is very low, typically 10%. At angles lower than 45°, some deviations from exponential are seen only for the slow relaxation.

The amplitude of the two components of the correlation function is  $a_p = a'_p / (a'_p + a'_c)$  and  $a_c = a'_c / (a'_p + a'_c)$  where:<sup>27</sup>

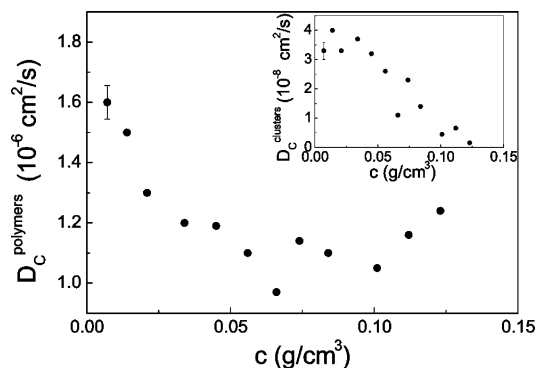
$$\begin{aligned} a'_p(Q) &= P_p(Q) S_p(Q) M_p c_p \\ a'_c(Q) &= P_c(Q) S_c(Q) M_c c_c \end{aligned} \quad (6)$$

with indexes *p* and *c* referring to polymers and clusters, respectively.

By comparing eq 6 and eq 3 and considering that  $I(Q) = I_p(Q) + I_c(Q)$ , the contribution of the polymers to the total scattered intensity is

$$I_p(Q) = \frac{I(Q)}{a_c/a_p + 1} \quad (7)$$

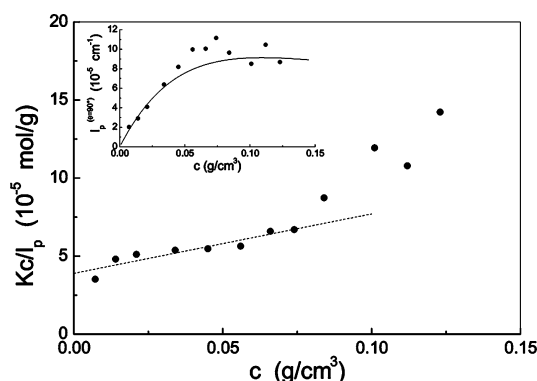
The collective diffusion coefficients obtained for polymers,  $D_c^{\text{polymers}}$ , and clusters,  $D_c^{\text{clusters}}$ , as a function of the UCS-NH<sub>2</sub>·HCl monomer concentration, are shown in Figure 2 and



**Figure 2.** Dependence of the collective diffusion coefficient ( $D_c$ ) of polymers from the mass concentration of UCS-NH<sub>2</sub>·HCl. That of clusters is reported in the inset.

in its inset, respectively. The relative mass percentage of monomers belonging to clusters can be estimated from the intensity fraction scattered from each component (considered as sphere) under the approximation that the mass density of both is similar. It is estimated to be about 0.05% at low concentrations, thus clusters are diluted enough to be regarded as not interacting with each other, especially for  $c < 0.05$  g/cm<sup>3</sup>, and their low amount is considered not to affect either the structural or dynamic properties of the polymers.

Although a decrease of  $D_c^{\text{polymers}}$  could, in principle, indicate an increase of the polymer molecular weight (and hence of the polymer size), in the present case this scenario is ruled out by the observed increase of the inverse of the normalized scattered intensity of polymers reported in Figure 3, which in the case of increasing polymer size would, instead, decrease. The initial trend of  $D_c^{\text{polymers}}$  as a function of concentration is rather ascribed to the effect of the interaction potential. By fitting the



**Figure 3.** Inverse of the normalized intensity scattered by polymers; the dashed line is the linear fit according to the virial expansion. The inset reports the intensity scattered by polymers along with the fit according to the Baxter's model (solid line).

polymers diffusion data with eq 2, in the low concentration region ( $c < 0.05$  g/cm<sup>3</sup>), the extrapolation to infinite dilution yields an hydrodynamic radius of polymers,  $R_H$ , of about 3 nm, and the slope gives a  $k_D$  value of about  $-7$  cm<sup>3</sup>/g.

At higher concentration ( $c > 0.05$  g/cm<sup>3</sup>),  $D_c^{\text{polymers}}$  seems to remain constant and hence to begin rising, as it happens for polymer solutions in the semidilute regime.<sup>28,29</sup>

To gain additional information on the interaction potential among polymers, the Debye plot reporting the inverse scattered intensity has to be considered. Owing to the presence of the larger aggregates, the  $Q$ -dependence of the scattered intensity is modulated by their form factor, then the virial expansion for the scattered intensity from polymers (for which  $P_p(Q) \approx 1$ ) obtained from equation eq 7 reads (in the low  $Q$  and  $c$  limits)

$$\frac{Kc}{I_p} = \frac{1}{M_p} [1 + 2A_2 M_p c] \quad (8)$$

From a linear fit of the inverse of the normalized scattered intensity of the polymers (shown in Figure 3), the molecular weight of the polymers formed,  $M_p \approx 25000$  Da (UCS-NH<sub>2</sub> monomer mass is 1390), and the static virial coefficient,  $A_2 = 1.9 \times 10^{-4}$  cm<sup>3</sup> mol/g<sup>2</sup>, are obtained. The positive value of  $A_2$  implies the presence of repulsive interaction among polymers. However, the equivalent hard-sphere radius,<sup>30</sup>  $S = [3M_w^2 A_2 / (16\pi N_A)]^{1/3}$ , used to represent the interparticle interactions in solution, is about 2 nm. The difference between  $S$  and  $R_H$  values, which is too large to be justified only by taking into account the hydration shell, indicates that repulsion is less than for hard-spheres. Due to such a small repulsion, friction interactions overcome the contribution of the static interaction and, as a result, the dynamic virial coefficient  $k_D$  becomes negative.

Under the hypothesis that polymers are noninteracting rigid rods, the  $A_2$  value would be consistent with the measured  $D_0$  only for rods with diameter of 0.3 nm, which is too small if considering the molecular size of UCS-NH<sub>2</sub>.

The comparison between  $S$  and  $R_H$  suggests, instead, the use of the Baxter's adhesive hard sphere model,<sup>8,31–34</sup> which describes the potential  $u(r)$  for a sphere of radius  $R$  as

$$\frac{u(r)}{k_B T} = \begin{cases} \infty & \text{for } 0 < r < R' \\ -\Omega & \text{for } R' < r < R \\ 0 & \text{for } R < r \end{cases} \quad (9)$$

where  $R-R'$  is the thickness of the adhesive layer and  $\Omega$  the adhesive potential. Baxter solved the Ornstein–Zernike equation<sup>35</sup> under the Percus–Yevik approximation,<sup>36</sup> in the limit that the thickness approaches to 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  $\phi$  and of the sticking parameter  $1/\tau$ .

Within this model, the structure factor at zero exchanged wave vector, expanded in powers of volume fraction, is<sup>33</sup>

$$\frac{1}{S(0)} = 1 + \left(8 - \frac{2}{\tau}\right)\phi + \frac{18\tau + 192\tau^3 - 90\tau^2 - 1}{6\tau^3}\phi^2 + \dots \quad (10)$$

with  $2/\tau$  in the linear term of eq 10 representing the “adhesive” contribution to the virial coefficient of a hard sphere. In order to compare the Baxter's model with the experimental data, it is necessary to introduce a relation between  $c$  and  $\phi$ . Assuming a

linear dependence as  $\phi = c/c^*$ ,  $c^*$  being the concentration at which spheres touch (identifiable with the overlap concentration of polymers<sup>26,28,29</sup>), then the static virial coefficient in the Baxter's model reads  $k_1 = (8 - 2/\tau)\phi/c$ .

As shown in the inset of Figure 3, the concentration dependence of the scattered intensity from polymers is well described by the Baxter's potential. This "adhesive" effect may derive from chloride-mediated ureido-ureido interactions<sup>37,38</sup> between different polymers (even though electrostatic interactions cannot be excluded).

The fit of the scattered intensity using eq 10 gives the same value for  $M_p$  as that found with the virial approach, the parameter  $1/\tau \approx 1.4$  and  $c^* = c/\phi \approx 0.05 \text{ g/cm}^3$ .

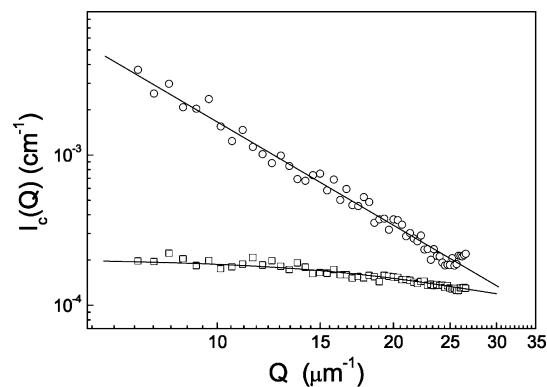
Although  $c^*$  does not define a sharp transition between the dilute and semidilute regime, we tried to use its definition ( $c^* = 3M_w/(4\pi N_A R_g^3)$ ) to estimate the polymer radius of gyration,  $R_g$ , which comes out to be about 6 nm. The  $R_g/R_H$  ratio is about 2 and, besides being in agreement with the rigid rod model previously excluded, is consistent with the value for a swollen random coil. The latter is, on its turn, consistent with the flexible nature of the 12-aminododecyl pendant group and with the spherical model involved in the Baxter potential.

One advantage of light scattering measurements consists in the possibility of investigating the dynamics and structure of clusters even if they are present in a low concentration. The value of  $D_c^{\text{clusters}}$  (reported in the inset of Figure 2) at low concentration gives a hydrodynamic radius for clusters of about 130 nm, which remains constant up to a concentration of  $0.07 \text{ g/cm}^3$ . The slowing down of the clusters diffusion upon increasing the monomer concentration is to be attributed to their progressively increasing hydrodynamic radius up to micrometric scale. This conclusion is based on the fact that, after centrifugation, the intensity scattered by the clusters at the highest concentration values significantly decreases.<sup>39</sup>

At the lowest concentration value and up to  $0.07 \text{ g/cm}^3$ , the scattered intensity profile (see Figure 4) is fitted with the homogeneous sphere form factor with radius  $R$ :<sup>40</sup>

$$P(Q) = \left[ \frac{3}{(QR)^3} (\sin(QR) - QR \cos(QR)) \right]^2 \quad (11)$$

In order to take into account the effect of the size polydispersity of clusters observed at low scattering angles, a



**Figure 4.** Representative data of the intensity scattered by clusters at two different concentration values (squares:  $c = 0.056 \text{ g/cm}^3$ ; circles:  $c = 0.12 \text{ g/cm}^3$ ). The solid curves referring to the low and high concentrations were fitted according to a homogeneous sphere form factor and a power law (with exponent  $-2.3$ ), respectively.

Gaussian size distribution function is introduced as the weight of the form factor. The fit with eq 11 gives for clusters a radius  $R \approx 150 \text{ nm}$ , in good agreement with the hydrodynamic radius, and a polydispersity of about 25%.

Above  $0.1 \text{ g/cm}^3$ , the intensity profile obeys a power law  $I(Q) \propto Q^{-D_f}$  with a fractal dimension  $D_f = 2.3$ , which suggests that clusters possess a fractal structure (grown by a diffusion limited aggregation mechanism).<sup>41,42</sup> This more tenuous cluster structure can be ascribed to a faster aggregation process favored by the higher concentration.

## CONCLUSIONS

Our findings highlight the key role played by the interaction pair potential on the stability of supramolecular polymers and the formation of clusters. Unlike the vast majority of linear supramolecular polymers, acid-promoted self-assembly of UC5-NH<sub>2</sub> is concentration independent. This trend is likely related to the coiled conformation of the polymer, which prevents the end-groups from being readily available for further self-assembly. This behavior has allowed us to gather indepth information on the polymer chain conformation as well as the interpolymer interaction potential.

The additional knowledge gained on the properties of this very promising class of polymers formed via noncovalent polymerization opens new perspectives from both a fundamental research viewpoint and in relation to future "smart material" development.

## ASSOCIATED CONTENT

### Supporting Information

Correlation functions at various concentration values,  $Q$ -dependence of the relative amplitude of fast and slow diffusion, and effect of centrifugation on clusters. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: villari@me.cnr.it.

### Notes

The authors declare no competing financial interest.

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