

# Dilute Solution Properties of Poly(dimethyldiallylammonium chloride) in Aqueous Sodium Chloride Solutions

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## SYNOPSIS

MW fractions of poly(dimethyldiallylammonium chloride) (PDMDAAC) were prepared by preparative size-exclusion chromatography and characterized by static and dynamic light scattering, viscometry, size-exclusion chromatography, and electrophoretic light scattering, in 0.50M NaCl solution. The behavior of fractions with  $MW < 2 \times 10^5$  was as expected for a strong polyelectrolyte in a good solvent, with a Mark-Houwink exponent of ca. 0.8, and MW-dependencies of the hydrodynamic radius and the radius of gyration of corresponding magnitude. At higher MW, curvature appears in the MW-dependencies, which can be best explained by the presence of branching. While this notably lowers the intrinsic viscosity at high MW, the electrophoretic mobility is unchanged regardless of molar mass. Thus, the branched polymers display the electrophoretic free-draining behavior characteristic of linear polyelectrolytes. © 1995 John Wiley & Sons, Inc.

**Keywords:** polyelectrolyte • poly(dimethyldiallylammonium chloride) • Mark-Houwink • branching

## INTRODUCTION

Poly(dimethyldiallylammonium chloride) (PDMDAAC) is an important commercial polycation, with a variety of applications in for example, water treatment and cosmetic formulations. The monomer readily undergoes cyclopolymerization to high MW<sup>1</sup> to yield a polymer of moderate linear charge density and no discernible hydrophobic character. Several reports have discussed the interaction of this polymer with different charged particles such as colloidal silica,<sup>2</sup> micelles,<sup>3</sup> and proteins.<sup>4-7</sup> Various studies have been devoted to an exploration of the molecular weight characterization of the polymer<sup>8-13</sup> with some inconsistencies possibly attributable to varying polydispersity. We report the determination of the weight-average molecular weight,  $M_w$ , the dispersity of MW,  $M_w/M_n$ , the radius of gyration,  $R_g$ , the hydrodynamic radius,  $R_h$ , the electrophoretic mobility,  $u$ , and the intrinsic viscosity,  $[\eta]$ , for PDMDAAC fractions in sodium chloride solutions by viscosity, size-exclusion chromatography, and light-scattering techniques.

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## EXPERIMENTAL

### Materials

Poly(dimethyldiallylammonium chloride), a commercial sample "Merquat 100" with nominal molecular weight of  $2 \times 10^5$  and polydispersity of  $M_w/M_n = 10$  was obtained from Calgon corporation (Pittsburgh, PA). The commercial sample was fractionated via size-exclusion chromatography (SEC) prior to use. The fractionation of PDMDAAC was carried out using a mobile phase of 0.5M NaNO<sub>3</sub> buffered with 25 mM NaOAc of pH 6.5, which has been found to sufficiently repress adsorption effects. We applied 40.0 mg of polymer to a Sephacryl S400 gel column via a 2.0 mL sample loop. The mobile phase was eluted through the column at a velocity of 2.0 mL/min, and the eluent was monitored using a R401 differential refractometer (Waters). The in-

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jected sample was separated into 30 fractions, collected at 4.8 mL intervals following the beginning of sample elution. All salts used in the present work were AR grades and obtained from Sigma. Distilled and deionized water was used in all experiments.

### Size-Exclusion Chromatography (SEC)

Analytical SEC was carried out on an apparatus comprised of a Minipump (Milton Roy), a model 7012 injector (Rheodyne) equipped with a 100  $\mu$ L sample loop, an R401 differential refractometer (Waters). A Superose-6 column (30  $\times$  1 cm OD) (Pharmacia) was eluted at 0.34 mL/min. Column efficiency, determined with acetone, was at least 12,000 plates/meter.

Injections were performed in a mobile phase of 0.5M NaCl and pH 6.5. The pH was maintained by 0.25M NaOAc buffer. Polymer samples (2.0 g/L) were filtered through Gelman 0.2  $\mu$ m syringe filters before injection.

### Viscosity

Viscosity measurements were carried out in a capillary viscometer of Ubbelohde type at temperature of 25  $\pm$  0.01°C. All solutions and solvents were filtered through Gelman 0.2  $\mu$ m syringe filters, prior to viscosity measurements. The intrinsic viscosities [ $\eta$ ] were determined from a common intercept of extrapolated zero polymer concentration in the Huggins plot. Solvent efflux time was 112.07 s for 0.5M NaCl. The precision of the efflux times was  $\pm$ 0.03 s.

### Quasi-Elastic Light Scattering (QELS)

QELS measurements were made at scattering angles of 30–150° with a Brookhaven (Holtsville, NY) 72 channel BI-2030 AT digital Correlator and using a Jodon 15 mW He-Ne laser (Ann Arbor, MI), or an air-cooled Ar<sup>+</sup> laser (200 mW). A 200  $\mu$ m pinhole aperture was used for the EMI photomultiplier tube, and decahydronaphthalene (Decalin) was used as the refractive index matching fluid to reduce stray light. We obtain the homodyne intensity-intensity correlation function  $G(q, t)$ , with  $q$ , the amplitude of the scattering vector, given by  $q = (4\pi n/\lambda)\sin(\theta/2)$ , where  $n$  is the refractive index of the medium,  $\lambda$  is the wavelength of the excitation light in a vacuum, and  $\theta$  is the scattering angle. For a Gaussian distribution of intensity profile of the scattered light,  $G(q, t)$  is related to the electric field correlation function  $g(q, t)$  by:

$$G(q, t) = A(1 + bg(q, t)^2) \quad (1)$$

where  $A$  is the experimental baseline and  $b$  is a constant, which depends on the number of coherence areas that generates the signal ( $0 < b < 1$ ). The quality of the measurements were verified by determining that the difference between the measured value of  $A$  and the calculated one was less than 1%. The electric field correlation function depends on the Fourier transform of the fluctuating number density of particles or molecules. For the center of mass diffusion of identical particles the following simple relation holds:

$$g(q, t) = e^{-t/\tau} \\ \frac{1}{\tau} = Dq^2 \quad (2)$$

where  $\tau$  is decay time and  $D$  is diffusion coefficient. In the present work, we use cumulant analysis to second order to obtain the relaxation time  $\tau$ . From each value of  $\tau$ , the diffusion coefficient can be calculated using

$$D = \frac{\lambda^2}{16\pi^2 \sin^2(\theta/2) \langle \tau \rangle} \quad (3)$$

and thus the Stokes' radius,  $R_s$ , by the Einstein equation

$$R_s = \frac{kT}{6\pi\eta D} \quad (4)$$

where  $k$  is Boltzmann's constant,  $T$  is the absolute temperature, and  $\eta$  is the viscosity of the solvent. In the present study the experimental uncertainty in  $R_s$  is less than 10%. More detailed discussions of QELS data analysis may be found in refs. 14 and 15.

### Static Light Scattering (SLS)

SLS measurements were made with the same Brookhaven system described above. Intensity measurements were calibrated by pure (> 99.5%) toluene and optical alignment was ensured by less than 2% deviation from linearity in the  $I \cdot \sin \theta$  vs  $\theta$  plot. Each measurement was carried out for 5 s. The average of 10 such measurements was reported as  $I_s$ . These values were used to calculate Rayleigh ratio,  $R_\theta$ .

To determine the molecular parameters of a macromolecule, static light-scattering results are

usually plotted as Zimm-diagrams corresponding to the equation:

$$\frac{Kc}{R_\theta} = \frac{1}{M_w} \left( 1 + \frac{16\pi^2}{3\lambda^2} R_g^2 \sin^2 \frac{\theta}{2} \right) + 2A_2c \quad (5)$$

where  $c$  is the mass concentration of polymer,  $K$  is a constant which contains the optical parameters of the system;  $M_w$  and  $R_g$  are the weight-average molecular weight and the root mean square radius of gyration of the macromolecule, respectively; and  $A_2$  is the second virial coefficient. For PDMDAAC, we used the refractive index increment,  $dn/dc = 0.186$ , determined by Burkhardt et al.<sup>11</sup> with a differential refractometer.

### Electrophoretic Light Scattering (ELS)

ELS measurements were made at four scattering angles (8.6, 17.1, 25.6, and 34.2°), using a Coulter (Hialeah, FL) DELSA 440 apparatus. The electric field was applied at 6.3 V/cm.

In ELS, the so called Doppler shift frequency,  $\Delta\omega$ , which is the difference between the angular frequency of the scattered light,  $\omega_s$ , and that of the reference beam,  $\omega_r$ , is measured.  $\Delta\omega$  is related to the electrophoretic mobility  $u$  ( $(\mu\text{m s}^{-1})/(V \text{cm}^{-1})$ ) by:

$$\Delta\omega = \frac{2\pi n}{\lambda} Eu \sin \theta \quad (6)$$

where  $E$  (volts/cm) is the applied electric field strength. Therefore,  $u$  can be directly evaluated from the frequency shift  $\Delta\omega$ . The  $u$  values obtained in this work are repeatable within 10%. Detailed discussion on ELS measurements can be found in ref. 16.

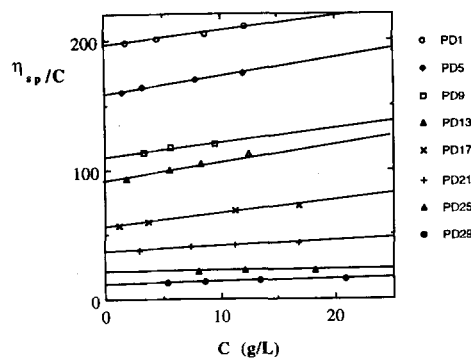


Figure 1. Viscosity plots for PDMDAAC fractions in 0.5M NaCl solutions.

### RESULTS AND DISCUSSION

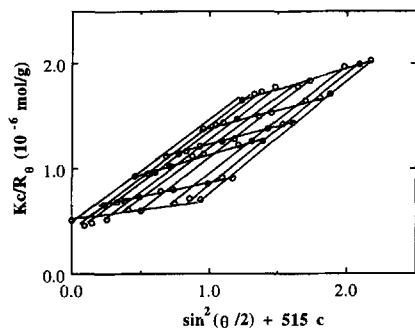
In order to suppress electrostatic expansion effects, most of the measurements were conducted in 0.5M NaCl. Figure 1 shows viscosity plots for the different fractions in this solvent at 25°C. The values of the intrinsic viscosity  $[\eta]$  for each fraction are obtained as the intercepts of plots in Figure 1 and summarized in Table I.

Figure 2 shows a typical example of Zimm plots of static light-scattering measurements for the sample PD1 in 0.5M NaCl solutions. From the Zimm plot, we obtain the weight-average molecular weight of  $M_w = 1.5 \times 10^6$  and the radius of gyration  $R_g = 55$  nm. The second virial coefficient  $A_2 = 2.53 \times 10^{-4} \text{ cm}^3 \text{ mol/g}^2$  was found to be independent of MW. Values of  $M_w$  and  $R_g$  for each fraction of PDMDAAC are given in Table I. Parallel QELS and ELS measurements were made at a polymer concentration of 1.0 g/L in 0.5M NaCl solutions. In view of the low polymer concentration we simply take the Stokes' radius,  $R_s$ , obtained from eq. (4)

Table I. Molecular Properties of PDMDAAC Fractions<sup>a</sup>

Sample	$M_w$	$[\eta]$ (mL/g)	$R_g$ (nm)	$R_h$ (nm)	$u$ ( $\mu\text{m cm/V-s}$ )
PD1	$1.5 \times 10^6$	$1.92 \times 10^2$	55	30	1.0
PD5	$1.2 \times 10^6$	$1.58 \times 10^2$	36	24	0.9
PD9	$3.9 \times 10^5$	$1.10 \times 10^2$	27	15	1.1
PD13	$2.3 \times 10^5$	89.6	26	13	0.9
PD17	$1.9 \times 10^5$	55.7	25	11	1.1
PD21	$7.8 \times 10^4$	36.5	17	7	1.0
PD25	$3.4 \times 10^4$	20.8	12	5	1.1
PD29	$1.5 \times 10^4$	11.2	10	4	1.2

<sup>a</sup> In 0.50M NaCl, at 25°C.



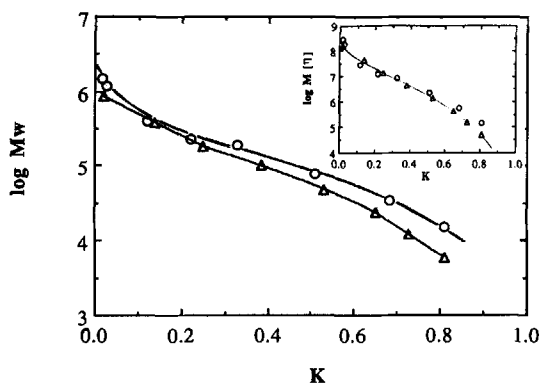
**Figure 2.** Typical  $Kc/R_\theta$  vs  $\sin^2(\theta/2)$  plot obtained for PD1 in 0.5M NaCl solution.

as the hydrodynamic radius,  $R_h$ , all QELS and ELS results are summarized in Table I.

The SEC calibration curve can be expressed as  $\log M_w$  vs. the chromatographic partition coefficient,  $K$ , which is defined as

$$K = \frac{V_e - V_o}{V_t - V_o} \quad (7)$$

where  $V_e$  is the solute retention volume,  $V_o$  the column void volume, and  $V_t$  the total permeable volume of the column.  $K$  may thus be viewed as the effective fraction of the pore volume to which the solute has complete access or, alternatively, as the equilibrium constant for the transfer of solute between the intrapore volume and the bulk solvent.  $V_o = 6.3$  mL, and  $V_t = 20.6$  mL were measured by elution of PEO ( $MW = 2 \times 10^6$ ) and  $D_2O$ , respectively. Figure 3 shows the calibration curve for PDMDAAC fractions. From the calibration curve, the MW dispersity,  $M_w/M_n$ , of each fraction was calculated and the



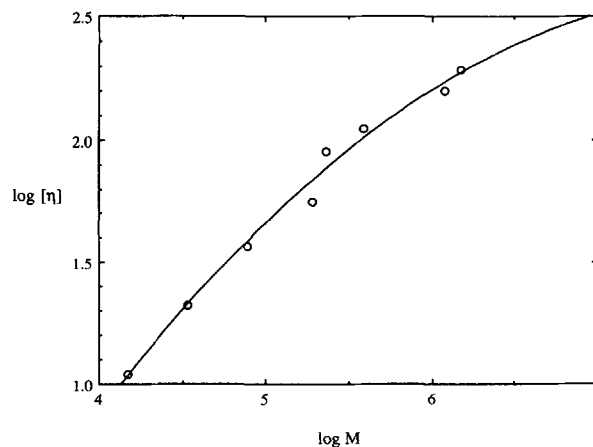
**Figure 3.** SEC calibration curve for PDMDAAC (○) in 0.5M NaCl solution. Calibration curve for pullulan (Δ) shown for comparison. Inset: "Universal Calibration" plot.

**Table II.** Characteristics of PDMDAAC Obtained by SEC

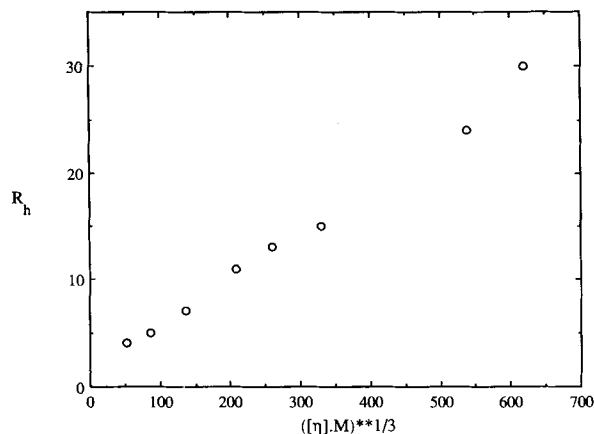
Sample	$M_w$	K	$M_w/M_n$
PD1	$1.5 \times 10^6$	0.016	1.09
PD5	$1.2 \times 10^6$	0.029	1.14
PD9	$3.9 \times 10^5$	0.12	1.20
PD13	$2.3 \times 10^5$	0.22	1.15
PD17	$1.9 \times 10^5$	0.33	1.21
PD21	$7.8 \times 10^4$	0.51	1.15
PD25	$3.4 \times 10^4$	0.68	1.20
PD29	$1.5 \times 10^4$	0.81	1.17

results are summarized in Table II. In the inset of Figure 3, the data for the PDMDAAC fractions and for pullulan fractions are compared using the "universal calibration" plot. While the plots for the two polymers are not completely congruent, there is no evidence of adsorption of the polycation on the gel, so it may be assumed that size separation is the predominant mechanism for the elution of PDMDAAC.

The double-logarithmic  $\bar{M}_w - [\eta]$  plot in 0.5M NaCl solution at 25°C shown in Figure 4 appears to display curvature. In order to ensure the quality of the data, comparison was made among the QELS, SLS and viscometry results, by plotting  $([\eta]M_w)^{1/3} \sim R_\eta$  (the viscosity radius) vs  $R_h$ , the hydrodynamic radius, obtained from the QELS-based diffusion coefficient. As seen in Figure 5, the correlation between  $R_h$  and  $R_\eta$ , with the exception of the highest MW datum, is excellent, which enhances our confidence in the three measurements. Turning to the SLS data, Figure 6 reveals that a plot of  $\log R_g$  vs  $\log M_w$  also displays downward curvature. This in-



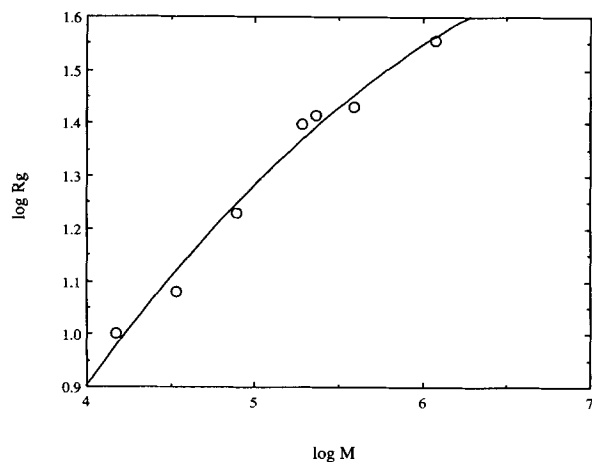
**Figure 4.**  $\log [\eta]$  versus  $\log M_w$  for PDMDAAC in 0.5M NaCl solution.



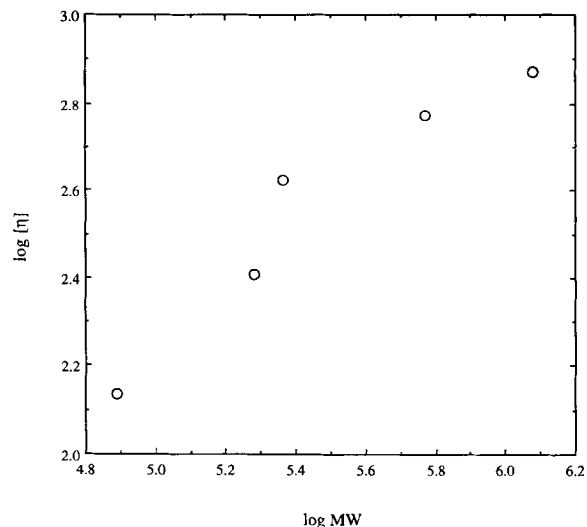
**Figure 5.** Log  $R_h$  versus  $\log([\eta]M_w)^{1/3}$  ( $\sim R_\eta$ ) for PDMDAAC in 0.5M NaCl solution.

indicates an increase in the mass : volume ratio with increasing MW.

The results of Figures 4–6 can be understood on the basis of branching in PDMDAAC. For fractions with  $M_w < 2 \times 10^5$ , the  $M - H$  exponent in 0.5M NaCl is 0.75, which is slightly lower than the values of  $a = 0.81$  and  $0.82$  for PDMDAAC in 1.0M NaCl reported, respectively, by Burkhardt<sup>11</sup> and by Wandrey et al.,<sup>10</sup> but higher than the value of 0.51 reported by Wyroba<sup>9</sup> in the same solvent. Considering the data for  $M_w > 2 \times 10^5$ , we obtain  $a \cong 0.4$ , which suggests branching at high MW. We carried out limited measurements of  $[\eta]$  in 0.01M NaCl, as shown in Figure 7 in which curvature is more prominent. The apparent slope below  $M_w \cong 2 \times 10^5$  is close to unity, which is reasonable for polyelectrolytes in highly dilute salt; but at higher MW the apparent value of  $a$  is about 0.5.



**Figure 6.** Log  $R_g$  versus  $\log M_w$  for PDMDAAC in 0.5M NaCl solution.

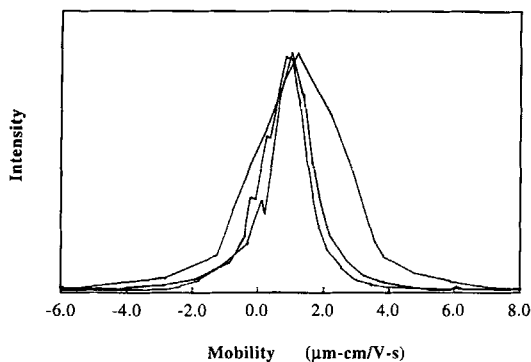


**Figure 7.** Log  $[\eta]$  versus  $\log M_w$  for PDMDAAC in 0.01M NaCl solution.

Wandrey and Görnitz have described several reactions undergone by DMDAAC during polymerization.<sup>13</sup> If only one double bond in DMDAAC reacts, the polymer also will contain linear monomer units with pendant double bonds which may serve as starting points for chain branching. Furthermore, Wandrey suggests that technical grade monomer may contain small amounts of methyltriallylammoniumchloride (MTAAC), a trifunctional monomer. By rigorous analysis of ultracentrifugation results, they were able to deconvolute the sedimentograms into contributions from linear and branched chains for polymer prepared with addition of MTAAC, but no such analysis was done for the high conversion product of technical grade monomer. Since relatively small amounts of branching have large effects on chain dimensions, and hence on viscosity, the Mark-Houwink exponent may be an even more sensitive measure of branching than ultracen-

**Table III.** Characteristic Constant  $\rho$  for PDMDAAC Samples

Sample	$M_w$	$\rho = R_g/R_H$
PD1	$1.5 \times 10^6$	1.8
PD5	$1.2 \times 10^6$	1.5
PD9	$3.9 \times 10^5$	1.8
PD13	$2.3 \times 10^5$	2.0
PD17	$1.9 \times 10^5$	2.3
PD21	$7.8 \times 10^4$	2.4
PD25	$3.4 \times 10^4$	2.4
PD29	$1.5 \times 10^4$	2.5



**Figure 8.** Typical electrophoretic light-scattering spectrum obtained for PD9 at scattering angles of 8.7, 26, and 34.2°.

trifugation. Since branching increases the number of growing chain ends, it is likely that branch sites will be concentrated in the higher-MW components, so curvature of the M-H plot is to be expected.

Hydrodynamic theory<sup>17</sup> shows that the characteristic constant  $\rho = R_g/R_h$  changes from infinity to 0.775 when the polymer structure changes from a long rod to a sphere. The random coil structure is believed to occupy an intermediate position between long rod and sphere. The light scattering results showed  $\rho$  between 1.5 and 2.5 as given in Table III. Particularly we note that the value of  $\rho$  is virtually constant for  $MW < 2 \times 10^5$  but then diminishes moderately in the direction of the sphere limit with increasing MW. This provides further evidence for growing molecular density in this MW series at high MW.

Figure 8 shows a typical electrophoretic light-scattering spectrum at different scattering angles for PD9 in 0.5M NaCl. The average frequency of the spectrum gives a mobility of 1.1  $\mu\text{m-cm/V-s}$ , as shown in Table I. The electrophoretic mobility is invariant with MW. It appears that the relatively modest branching, to which the intrinsic viscosity is quite sensitive, does not alter the electrophoretically free-draining behavior of the PDMDAAC fractions. On the other hand, the viscometric behavior, for which case solvent drag is not compensated for by counterion flow, corresponds to that expected for partially nondraining polymers.

In summary, fractions of commercial PDMDAAC in 0.5M NaCl solution were characterized by techniques of light scattering, viscometry, and size-exclusion chromatography. Below  $MW \cong 2 \times 10^5$ , the polymer behaves as a typical statistical chain poly-

electrolyte in a good solvent; at higher MW, branching depresses the intrinsic viscosity and the radius of gyration.

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