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## **SOLUTION PROPERTIES AND CHAIN STIFFNESS OF POLY(ACENAPHTHYLENE)**

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**Key Words:** Poly(acenaphthylene); Unperturbed dimensions; Chain stiffness

### **ABSTRACT**

Solution properties of poly(acenaphthylene) (PACN) were investigated in a theta solvent (1,2-dichloroethane) and a good solvent (chloroform). The viscosity exponent  $\alpha$  was found to be 0.50 at both 35 and 41°C in 1,2-dichloroethane. Unperturbed dimensions found from viscometric measurements were compared with those of other vinyl aromatic polymers. Calculation of the chain flexibility parameters led to the conclusion that PACN is a rather stiff chain compared to other vinyl polymers with its characteristic ratio  $C_\infty$  of 18.2 and chain flexibility parameter  $\lambda$  of 7.

### **INTRODUCTION**

The solution properties of poly(acenaphthylene) (PACN) are of interest because it is expected to have a highly stiff chain for a vinyl polymer. The stiffness is caused by steric hindrance to internal rotation due to the bulky naphthalene substituent and, perhaps more importantly, because every other C—C bond in the backbone is locked so that molecular rotation of these bonds is impossible.

A number of studies on the dilute solution properties of PACN have appeared [1-4], but the discrepancies among the results are rather surprising. Moaconin et al. [1] reported the viscosity exponent of PACN in 1,2-dichloroethane (DCE) at 35°C to be 0.50 whereas Barrales-Rienda and Pepper [2, 3] found this exponent to be 0.54 in the same solvent at 25°C. They reported the  $\theta$  temperature in DCE to be 20°C based on their critical solution temperature measurements. More recently, Agbafé and Springer [4] reported the  $\theta$  temperature of PACN in DCE to be 39.2°C for branched and 41.1°C for linear samples based on the temperature dependence of the second virial coefficient as determined by light-scattering experiments.

No unified conclusion related to the unperturbed dimensions and chain rigidity of PACN chains can be drawn from the results of previous work.

Moaconin et al. [1] and Barrales-Rienda and Pepper [2, 3] concluded that PACN chains are more flexible than expected, whereas Tsvetkov et al. [5] assessed the Kuhn segment of PACN to be twice as large as those found for the usual flexible chain polymers, which indicates the rigidity of the chain.

In a previous paper we presented some experimental data for the in-source and postirradiation polymerization of acenaphthylene in the solid state [7]. For the present study we investigated PACN in a  $\theta$  solvent [1,2-dichloroethane (DCE)] and in a good solvent [chloroform (CHL)]. The unperturbed dimensions and chain flexibility parameters were calculated and compared with those of polystyrene and other vinyl aromatic polymers.

## EXPERIMENTAL

### Materials

Acenaphthylene was a product of the BDH Company. It was purified by recrystallization thrice from ethanol. After acenaphthylene was dried in a vacuum oven, the melting point of the crystals was found to be 92-92.5°C. 1,2-Dichloroethane was a product of the Merck Company. It was distilled over  $\text{Al}_2\text{O}_3$  under vacuum just before use. Toluene and chloroform were pure analytical grade materials. They were used without further purification. Methanol and ethanol were distilled prior to use.

### In-Source Polymerization

Monomer was placed into Pyrex polymerization tubes, degassed under vacuum, and sealed under a pressure of  $10^{-4}$ - $10^{-5}$  torr. The sealed tubes were irradiated with Co-60 gamma rays at room temperature. The dose rate was 0.65 kGy/h. After a certain polymerization time, the inner contents were dissolved in toluene and poured into excess methanol. The polymers were collected by filtration, then vacuum dried to constant weight.

### Thermal Polymerization by Free Radical Initiator

Known amounts of monomers and benzoyl peroxide were placed into Pyrex polymerization tubes. They were degassed and sealed under vacuum. The polymeriza-

tion was carried out at 100°C. The polymers were obtained by dissolving the reaction mixture in toluene, precipitating with methanol, and drying in a vacuum oven.

### Size Exclusion Chromatography (SEC)

The molecular weight distribution of the polymers was determined by using Waters Associate Model 200 Gel Permeation chromatography (or SEC). The instrument has Styragel columns with  $10^5$ ,  $10^4$ ,  $5 \times 10^3$ ,  $10^3$ , and 10 nm pore sizes. Toluene was used as the solvent at a flow rate of 1.0 mL/min and at a temperature of 45°C. The universal calibration method was used to evaluate the average molecular weights.

### Viscometry

Viscosity measurements were carried out in toluene, DCE, and chloroform by using a Ubbelohde-type viscometer. The temperature was kept constant to  $\pm 0.1^\circ\text{C}$ . Kinetic energy corrections were negligible. Intrinsic viscosities were obtained by simultaneous extrapolation of  $\eta_{sp}/c$  and  $\ln \eta_r/c$  to infinite dilution. In order to avoid any possible photodegradation, the solutions were prepared not more than one day before the measurements were made. Because this polymer is light sensitive [6], prolonged exposure to light was avoided.

## RESULTS AND DISCUSSION

Table 1 shows the characteristics of the samples used in this study. Samples coded as R were synthesized via in-source polymerization with gamma irradiation. It was not possible to obtain polymers with molecular weights higher than about  $7 \times 10^4$  with this method. By increasing the polymerization time beyond 2300 hours (total irradiation dose higher than 1500 kGy), a decrease in molecular weight occurred, possibly due to chain scission [8].

TABLE 1. Molecular Characteristics of Poly(Acenaphthylene)

Sample	$M_n \times 10^{-4}{}^a$ g·mol <sup>-1</sup>	$M_w \times 10^{-4}{}^a$ g·mol <sup>-1</sup>	$M_v \times 10^{-4}{}^b$ g·mol <sup>-1</sup>	$M_w/M_n$
R10	1.50	4.76	3.85	3.2
R5	—	—	4.60	—
R6	2.00	6.75	6.30	3.4
R8	2.10	7.30	7.10	3.5
T4	5.30	15.8	14.8	3.0
T3	7.90	35.4	29.8	4.5
T2	17.2	71.6	59.0	4.1
T1	33.0	119	116	3.6

<sup>a</sup>Determined by SEC.

<sup>b</sup>Determined by viscometry.

In order to obtain samples of higher molecular weight, radical polymerization was carried out at 100°C. Samples coded as T were obtained by this method. The  $M_w$  and  $M_n$  values listed in Table 1 were evaluated from SEC chromatograms by using the universal calibration method. Standard polystyrene samples with very narrow molecular weight distributions were used for universal calibration. Also included in Table 1 are viscosity-average molecular weights,  $M_v$ , calculated from the following Mark-Houwink-Sakurada (MHS) equation given by Agbafé and Springer [4].

$$[\eta] = 8.64 \times 10^{-3} M_v^{0.65} \quad (\text{in toluene at } 28^\circ\text{C})$$

The UV absorption spectra of the polymers obtained by both  $\gamma$ -radiation and radical polymerization methods show maximum absorption at the same wavelength,  $\lambda_{\max} = 297$  nm, whereas for the monomer,  $\lambda_{\max} = 323.6$  nm (Fig. 1). The polydispersity ratios of the samples are also close to one another, as can be seen from Table 1. Furthermore, the points in double logarithmic plots of  $[\eta]$  versus  $M_v$  in DCE and in CHL (Fig. 2) fall on the same straight line. This indicates that there is essentially no difference in the structure of the polymers obtained by radiation and by thermal methods.

Chloroform was found to be a good solvent for PACN (Fig. 3). Although chloroform is similar in structure to DCE, its dielectric constant (4.77) is lower than that of DCE (10.52) [9]. For that reason it acts as a better solvent for nonpolar PACN. The intrinsic viscosities in CHL were measured at 25°C. The data from all the intrinsic viscosity measurements are collected in Table 2. As can be seen from this table, there is a very slight increase in  $[\eta]$  values in DCE when the temperature is increased from 35 to 41°C. A least-squares analysis of the intrinsic viscosity data gives the following MHS equations, where  $[\eta]$  is in  $\text{cm}^3/\text{g}$ .

$$[\eta] = 3.81 \times 10^{-2} M_v^{0.50} \quad (\text{in DCE at } 35^\circ\text{C})$$

$$[\eta] = 4.15 \times 10^{-2} M_v^{0.50} \quad (\text{in DCE at } 41^\circ\text{C})$$

$$[\eta] = 6.77 \times 10^{-3} M_v^{0.68} \quad (\text{in DCE at } 25^\circ\text{C})$$

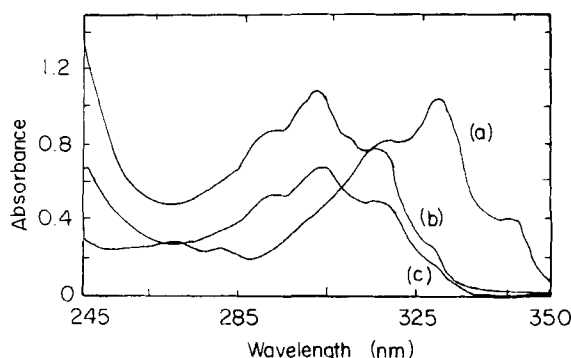


FIG. 1. UV absorption spectra of (a) acenaphthylene, (b) poly(acenaphthylene) synthesized by  $\gamma$ -irradiation polymerization, and (c) PACN synthesized by thermal polymerization initiated by benzoyl peroxide.

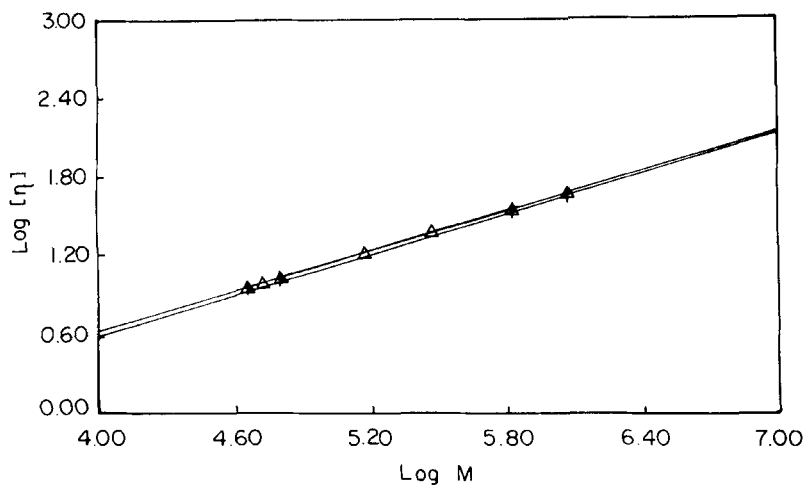


FIG. 2. Double logarithmic plots of  $[\eta]$  versus  $M_v$  for PACN samples in DCE at 35°C (+) and at 41°C ( $\Delta$ ).

Although  $K_\theta$  values differ slightly, the exponent  $\alpha$  was found to be the same (0.50) at 35 and 41°C in DCE. This indicates that the coil-globule transition does not occur sharply but over a temperature interval in the ACN-DCE system. We observed a similar behavior for poly(*p*-*tert*-butylstyrene) in the  $\theta$  solvent 1-nitropropane [10]. This result was attributed to the steric effect of the side group, which is also the case for PACN.

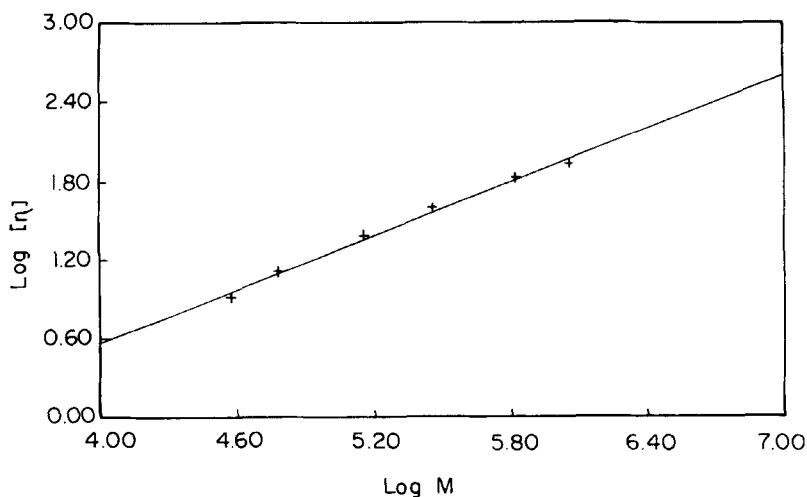


FIG. 3. Double logarithmic plot of  $[\eta]$  versus  $M_v$  for PACN samples in chloroform at 25°C.

TABLE 2. Intrinsic Viscosities of PACN Samples<sup>a</sup>

Sample	$[\eta]_{\text{TOL}}^{25^\circ\text{C}}$	$[\eta]_{\text{DCE}}^{35^\circ\text{C}}$	$[\eta]_{\text{DCE}}^{41^\circ\text{C}}$	$[\eta]_{\text{CHL}}^{25^\circ\text{C}}$
R10	8.25	—	—	8.48
R5	9.27	7.99	8.98	—
R6	10.15	—	9.46	—
R9	11.34	10.32	10.77	13.07
R8	12.32	—	—	—
T4	19.84	—	15.97	24.64
T3	31.20	—	23.80	39.22
T2	53.64	33.35	35.30	67.90
T1	75.74	41.55	44.48	86.25

<sup>a</sup>In  $\text{cm}^3 \cdot \text{g}^{-1}$ . TOL = toluene, DCE = 1,2-dichloroethane, CHL = chloroform.

The unperturbed dimensions of polyacenaphthylene were determined under  $\theta$  conditions by using the Flory–Fox equation [11].

$$[\eta]_{\theta} = K_{\theta} M^{0.50} \quad (1)$$

where

$$K_{\theta} = \phi_0 \left( \frac{\langle r^2 \rangle_{\theta}}{M} \right)^{3/2} \quad (2)$$

and also from intrinsic viscosity data in a good solvent by using the Buchard–Stockmayer–Fixman (BSF) equation [12, 13].

$$[\eta]/M^{1/2} = K_{\theta} + 0.51BM^{1/2} \quad (3)$$

where  $B$  is a parameter characterizing long-range interactions. Figure 4 gives a BSF plot for PACN in CHL at 25°C. Because CHL is a very good solvent for PACN, this plot deviates from linearity. The nonlinear regression of the experimental points give  $K_{\theta} = 4.07 \times 10^{-2} \text{ cm}^3/\text{g}$ . This value of  $K_{\theta}$  is in good agreement with  $K_{\theta}$  in DCE at 41°C ( $4.15 \times 10^{-2} \text{ cm}^3/\text{g}$ ).

The unperturbed dimensions were calculated from  $K_{\theta}$  by using the equation [11]

$$\frac{\langle r^2 \rangle}{M} = \left( \frac{K_{\theta}}{\phi} \right)^{2/3} \quad (4)$$

The applicable value of  $\phi$  at the  $\theta$  point or at the near- $\theta$  point is  $\phi_0 = 2.5 \times 10^{23}$  for monodisperse polymers [14]. For heterodisperse polymers, a reasonable estimate of an average value of the Flory viscosity function can be made by using [14]

$$Q(\epsilon) = \phi_{\text{av}}/\phi_0 \quad (5)$$

This quantity depends on the distribution function of the molecular weights and the solvent power. The solvent power is characterized by the parameter  $\epsilon$ :

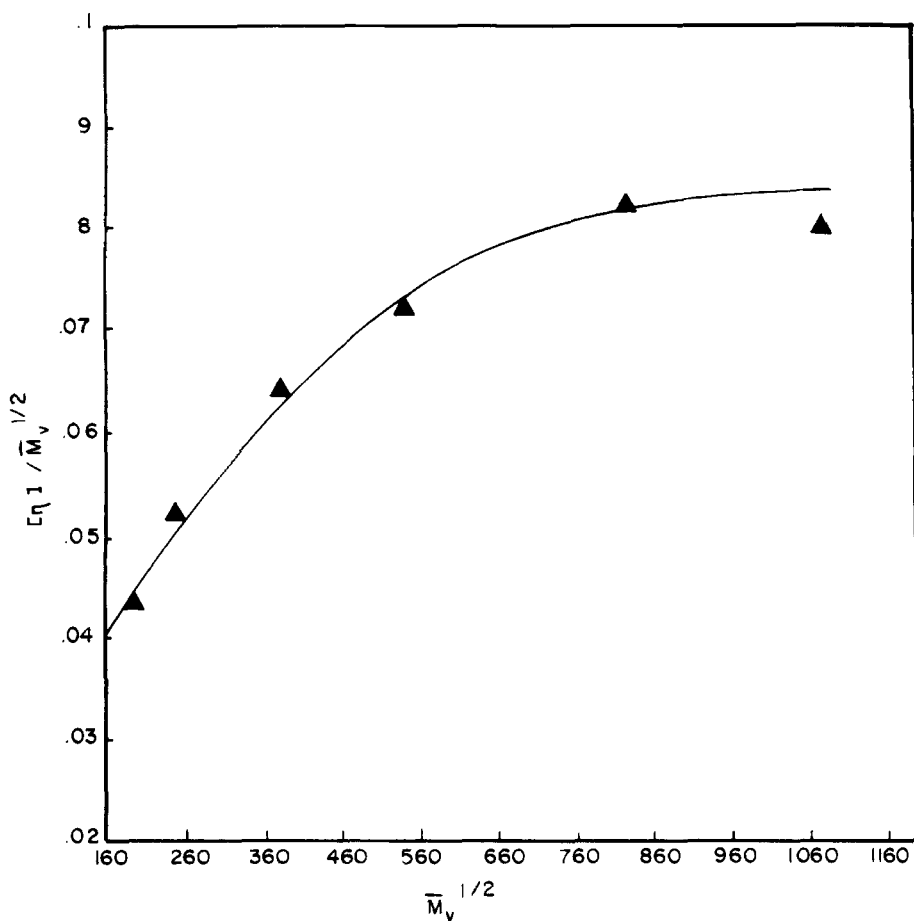


FIG. 4. BSF plot in chloroform at 25°C.

$$\epsilon = (2\alpha - 1)/3 \quad (6)$$

where  $\alpha$  is the MHS exponent.

If the molecular weight distribution is approximated by the Schulz-Zimm distribution with parameter  $b$ , where

$$\frac{1}{b} = \frac{M_w}{M_n} - 1 \quad (7)$$

$Q(\epsilon)$  is given by

$$Q(\epsilon) = (b + 1) \frac{\Gamma\left(b + \frac{3}{2} + \frac{3}{2}\epsilon\right)}{\Gamma(b + 1)} \left( \frac{\Gamma(b + 2)}{\Gamma(b + 3 + \epsilon)} \right)^{3/2} \quad (8)$$

where  $\Gamma$  is the generalized factorial function (gamma function).



For  $\theta$  conditions,  $\epsilon = 0$ . By using the average value of  $M_w/M_n = 3.5$  (Table 1),  $Q(0) = 0.408$ , and Eq. (5) gives  $\phi_{av} = 1.02 \times 10^{23}$ .

A similar correction of  $\phi$  was carried out in chloroform. An MHS exponent of  $\alpha = 0.68$  gives  $\epsilon = 0.12$  (Eq. 6). Therefore,  $Q$  is 0.36, which leads to  $\phi_{av} = 9.05 \times 10^{22}$ .

In previous papers on the dilute solution properties of PACN, the  $\phi$  value was also corrected [15]. Moaconin et al. [1] and Tsvetkov et al. [5] used corrected  $\phi_0$  values of  $1.4 \times 10^{23}$  and  $1.8 \times 10^{23}$ , respectively.

These  $\phi_{av}$  values were used in Eq. (4) as  $\phi$  to obtain the  $\langle r^2 \rangle / M$  value. The results are tabulated in Table 3. The steric factors ( $\sigma$ ) in Table 3 were calculated from

$$\sigma = \left( \frac{\langle r^2 \rangle_0 / M}{\langle r^2 \rangle_{0,f} / M} \right)^{1/2} \quad (9)$$

where  $(\langle r^2 \rangle_{0,f} / M)^{1/2}$  is the unperturbed dimensions for a freely rotating chain and has a value of  $2.50 \times 10^{-9}$  cm for PACN. It can be seen from Table 3 that the  $\sigma$  values found in the present study are greater than those reported for PACN in previous studies. That can be because they were studied at temperatures (20 and 35°C) slightly below the  $\theta$  temperature (41.1°C in DCE by our estimate). Our  $\sigma$  value is close to that reported for poly( $\beta$ -vinylnaphthalene). Since both polymers have nearly identical bulky side groups, the higher  $\sigma$  value we found seems reasonable.

Flory's characteristic ratio can be calculated from  $(\langle r^2 \rangle_0 / M)$  according to the equation [16]

$$C_\infty = \lim_{n \rightarrow \infty} \frac{\langle r^2 \rangle_0}{nl^2} = \frac{\langle r^2 \rangle_0}{M} \frac{M_0}{l} \quad (10)$$

where  $M_0$  is the monomer molecular weight and  $l$  is the bond length ( $l = 1.58 \times 10^{-8}$  cm). Larger  $C_\infty$  values reflect increased hindrance to rotation about main-chain bonds. Taking  $(\langle r^2 \rangle_0 / M)$  as  $5.68 \times 10^{-17}$  cm<sup>2</sup> (the average value from Table 3), we found  $C_\infty = 18.2$  for PACN. When this value was compared with the characteristic ratio of polystyrene [16] ( $C_\infty = 10.2$ ), we concluded that PACN has a much less flexible chain than does polystyrene.

The viscosity data were also analyzed in terms of the Kratky-Porod wormlike chain model. The Kuhn statistical segment length  $A$  was calculated from [17]

$$A = \frac{\langle r^2 \rangle_0}{M} \frac{M_0}{h} \quad (11)$$

where  $h$  is the monomer unit projection length. Gonzales et al. [18] experimentally determined  $h = 2.53 \times 10^{-8}$  cm for PACN from SEC and viscometry studies. This value is in agreement with that calculated by Tsvetkov et al. [5], assuming a *trans*-disyndiotactic configuration. By taking  $h = 2.53 \times 10^{-8}$  cm and  $\langle r^2 \rangle_0 / M = 5.68 \times 10^{-17}$  cm<sup>2</sup>, the Kuhn statistical segment length  $A$  was found to be  $34 \times 10^{-8}$  cm for PACN. Dividing this value of  $A$  by the monomer unit projection length  $h$ , we obtained the number of units per statistical segment as 14. This number is almost twice as large as that reported for polystyrene, 7.6 [19].

TABLE 3. Unperturbed Dimensions and the Steric Factor  $\sigma$  for Poly(Acenaphthylene) and for Some Other Vinyl Aromatic Polymers

Polymer	Solvent	$T$ , °C	$K_\theta \times 10^{-2}$ cm <sup>3</sup> /g	$\left(\frac{\langle r^2 \rangle_0}{M}\right)^{1/2 a}$	$\left(\frac{\langle r^2 \rangle_{0,f}}{M}\right)^{1/2 a}$	$\sigma$	Reference
PACN	DCE	20	2.12	5.20	2.50	2.1	2
PACN	DCE	35	4.56	6.00	2.50	2.4	1
PACN	DCE	41.1	4.27	—	—	—	4
PACN	DCE	41	4.15	7.41	2.50	3.0	This work
PACN	CHL	25	4.07	7.66	2.50	3.1	This work
PS <sup>b</sup>	Cyclohexane	34	8.20	6.70	3.02	2.2	22
P2VN <sup>c</sup>	Decalin/toluene	30.2	5.20	8.10	2.49	3.2	23

<sup>a</sup>cm<sup>3</sup>·mol<sup>1/2</sup>·g<sup>-1/2</sup>.<sup>b</sup>Polystyrene.<sup>c</sup>Poly(2-vinylnaphthalene).

Ptitsyn and Eizner proposed the  $\lambda$  parameter as a measure of chain flexibility and suggested  $\lambda = 4$  as a boundary between rigid and flexible macromolecules.  $\lambda$  is defined as [20]

$$\lambda = a/h \quad (12)$$

where  $a$  is the persistence length ( $a = A/2$  for random flight chains). Our viscosity results give a Ptitsyn–Eizner flexibility parameter of  $\lambda = 7$ . Leon et al. [21] report  $\lambda = 6.3$  for poly(*n*-vinylcarbazole) in the unperturbed state. When these two values (and other values reported in the literature [13]) are compared, it can be seen that PACN is less flexible than PNVC and most other vinyl aromatic chains.

## CONCLUSIONS

1. For PACN, the viscosity exponent is 0.50 in DCE in the temperature interval 35–41°C. Therefore, in this temperature interval, PACN remains at an almost unperturbed state. The transition from coil to globule is not sharp.

2. PACN is a semirigid chain with a Ptitsyn–Eizner flexibility parameter of  $\lambda = 7$  and  $C_\infty = 18.2$  as expected from its bulky side groups and locked main chain bonds.

## ACKNOWLEDGMENT

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