UNPERTURBED DIMENSIONS OF ATACTIC POLY(PHENYLACETYLENE)

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Dedicated to our great friend and colleague Dr. Marta Pacovská who left us for ever a year ago.

Dilute solution characteristics of atactic (ca. 30% *trans*) poly(phenylacetylene), PPA, were determined by using the SEC/MALS technique in order to obtain a deeper insight into discrepancy between presumed rigidity of conjugated polyvinylene molecules and their random-coil behavior in solutions resulting from earlier viscometry measurements. PPA was found to exhibit the molecular-weight dependence of the radius of gyration in tetrahydrofuran solution similar to that of atactic polystyrene (saturated analogue of PPA); also unperturbed dimensions of these polymers are almost equal. This rather surprising observation is explained as a consequence of the increased π–π attraction between highly polarizable PPA segments with well-delocalized π-electrons, which compensates the effect of stiffening of these segments due to conjugation. Possible influence of chain branching is also discussed.

Keywords: Polyacetylenes; Polyphenylacetylene; Polyvinylenes; Radius of gyration; Scaling law; Unperturbed dimensions; Polymers; Conformation analysis.

Knowledge of conformations and dimensions of polyvinylene-class molecules in solutions is rather poor although these polymers have been investigated for almost three decades[1]. The dilute-solution characteristics of polyvinylenes published in literature are summarized in Table I. Those are mainly values of the constants a and K_η of the Kuhn–Mark–Houwink–Sakurada (KMHS) equation

$$[\eta] = K_\eta M^{a} \qquad (1)$$

which have been determined for eleven polyvinylenes[2–7] ([η] is the limiting viscosity number and M the molecular weight of the polymer), and values of the characteristic ratio C_∞

$$C_\infty = \left(\langle R^2\rangle_0 / nl^2\right)_{n\to\infty} = \left(6\langle S^2\rangle_0 / nl^2\right)_{n\to\infty} \qquad (2)$$

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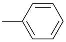
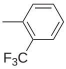
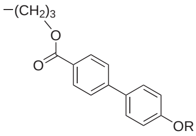
recently determined[7] for four polyvinylenes differing in the length of pendant groups only ($\langle R^2 \rangle_0$ is the mean-square end-to-end distance and $\langle S^2 \rangle_0$ the mean-square radius of gyration of a linear macromolecule in the unperturbed state (denoted by the subscript $_0$), n the number of main-chain skeletal bonds and l the mean length per skeletal bond).

TABLE I
Values of KMHS constants (Eq. (*1*)) and characteristic ratio C_∞ of substituted polyacetylenes $[–CR^1=CR^2–]_n$ published in literature

R^1	R^2	Solvent, temperature	10^3 K_η ml/g	a	Ref.	Note, method[a]
Ph	Me	toluene, 30 °C	2.00	0.89	2	LS + visco
Ph	Et	toluene, 30 °C	3.39	0.92	2	LS + visco
Ph	hept-1-yl	toluene, 30 °C	0.24	1.15	2	LS + visco
Ph	Cl	THF, 38 °C	0.55	0.85	3	LS + visco
		toluene, 30 °C	0.087	1.07	4	
H	*tert*-Bu	toluene, 30 °C	0.76	1.01	5	54–78% *cis* $\langle M \rangle_n$, osmometry+visco
H		THF, 30 °C	24.8	0.61	6	73% *cis*
			30.6	0.59		58% *cis* hyphen. SEC/visco/LALS
H		THF, 38 °C	2.7	0.59	3	LS + visco
		toluene, 30 °C	21	0.60		
H		THF, 25 °C	31	0.50	7	R = but-1-yl; C_∞ = 21.0[b]
			12	0.60		R = pent-1-yl; C_∞ = 21.0
			2.3	0.75		R = hept-1-yl; C_∞ = 16.0
			22.0	0.53		R = non-1-yl; C_∞ = 24.0 hyphen. SEC/visco/RALS

[a] visco, viscometry or viscometric detector; LS, light scattering; LALS, low-angle light scattering detector; RALS, right-angle light scattering detector. [b] Determined from a correlation of the limiting viscosity number with molecular weight of the polymer using the Stockmayer–Fixman equation[10]

Values of the KMHS exponent *a* found for polymers of disubstituted acetylenes and poly(*tert*-butylacetylene) are close to 1, as expected for rigid macromolecules. Delocalization of π-electrons along the chain backbone should significantly reduce internal rotations along main-chain single bonds bringing about stiffening of macromolecules. This restriction is supposed to be high enough to give rise to the cisoid-transoid (*cis*-like and *trans*-like) isomerism of polyvinylene chains[1e,8]. However, *a* values from 0.50 to 0.75 found for poly(phenylacetylene) (PPA), poly{[(2-trifluoromethyl)phenyl]acetylene}, and polymers of monosubstituted acetylenes with pendant groups $–(CH_2)_3OOC–C_6H_4–C_6H_4–OR$ (R is *n*-alkyl C_4, C_5, C_7 and C_9, respectively) occur in the region typical of flexible macromolecules, which strongly contradicts to an assumed increase in the chain dimensions due to conjugation. This suggests that the steric effects of substituents, but not the main-chain conjugation, are responsible for the rigidity of molecules of poly(*tert*-butylacetylene) and polymers of disubstituted acetylenes. It is worth mentioning that published values of C_∞ (20 ± 4, see Table I) are quite high, thus being not in accordance with values of the exponent *a* found for the same polymers. This can be ascribed to too low values of the degree of polymerization (DP) of studied polymers[7] (DP intervals from 90–220 to 150–320), since C_∞ is defined as a limiting quantity for infinite chains.

To obtain more reliable values of C_∞ for monosubstituted polyvinylene chains, we decided to determine this quantity for atactic, high-molecular-weight PPA. As polymers of monosubstituted acetylenes are known to degrade in solutions[9], we have chosen the SEC/MALS method (SEC – size exclusion chromatography; MALS – multiangle light scattering detector), which provides time-consistent pairs of values of M and $\langle S^2 \rangle^{1/2}$ for almost molecularly uniform polymer fractions, which can easily be evaluated according to relations arising from the theory of dilute polymer solutions[10,11]. The SEC/MALS method is of increasing importance in this field because, as was demonstrated in recent years[12], it provides sufficiently precise data (even for degrading polymers[13]) from which reliable values of unperturbed dimensions of polymer molecules can be calculated. Results of this investigation are presented in the present paper.

EXPERIMENTAL

Atactic, *cis*,*trans*-PPA was prepared by the metathesis polymerization of phenylacetylene with $WOCl_4/Ph_4Sn$ catalyst system in the mixed benzene/1,4-dioxane (1:1 by volume) solvent using standard break-seals vacuum technique and the procedure described earlier[14]. An orange-red, well soluble *cis*,*trans*-PPA was obtained, which contained 72% of *cis* units as determined by ^{1}H NMR. The dried polymer was stored under vacuum in a sealed glass ampoule.

SEC/MALS analyses were performed at 25 °C using a Perkin–Elmer chromatograph equipped with a differential refractometer (Waters R 401) and MALS Dawn-DSP photogoniometer (Wyatt Technology Corporation) as detectors. A series of three PL-gel columns (10^5, 10^3, 5×10^2) and HPLC-grade tetrahydrofuran (THF) as eluent (flow rate 1 ml/min) were used. The MALS device was operating at $\lambda = 633$ nm (He-Ne laser) at which the PPAs studied did not absorb. It was calibrated with spectroscopic grade toluene; normalization of detectors as well as a determination of the inter-detector volume was done using almost molecularly uniform PS standards (M below 50 000) that do not show an angular dependence of scattered light. The MALS and RI data were evaluated using the WTC Astra 4.50 software and the Zimm plot method to obtain absolute value of the z-average root mean square radius of gyration $\langle S^2\rangle_z^{1/2}$ and weight-average molecular weight $\langle M\rangle_w$ for each PPA fraction pertaining to a particular slice of SEC record. These values were further treated as $\langle S^2\rangle^{1/2}$ and M values of formally molecularly uniform polymer samples.

A solid PPA sample was taken from vacuum just before starting SEC analysis, dissolved in THF (concentration 10 mg/ml) and, after 15 min, the solution (100 μl) was injected into the SEC system. This time is sufficient for complete molecular dissolution of high-molecular-weight PPA, as it was demonstrated in our previous studies[9,14b]. The stock solution was allowed to stand in air; slow degradation of dissolved PPA provided a series of practically identical PPA samples of gradually lowered molecular weights (Table II).

TABLE II

Molecular-weight characteristics and scaling-law constants of studied PPA samples and scaling-law constants for the radius of gyration, S, and hydrodynamic radius, S_h, of polystyrene (PS)[15]; THF, 25 °C

PPA sample	10^{-3} M_n	10^{-3} M_w	10^{-3} M_z	log K	K, nm	σ	Correl. coef.
A	150	258	382	–1.904	$1.25 \cdot 10^{-2}$	0.588	0.9998
B	131	219	322	–1.931	$1.17 \cdot 10^{-2}$	0.592	0.9997
C	116	193	280	–1.845	$1.43 \cdot 10^{-2}$	0.578	0.9998
D	102	166	239	–1.939	$1.51 \cdot 10^{-2}$	0.594	0.9997
E	98	155	230	–1.783	$1.65 \cdot 10^{-2}$	0.567	0.9994
Average	–	–	–	–1.870	$1.35 \cdot 10^{-2}$ [a] $(1.40 \cdot 10^{-2})$[b]	0.584	0.9997
PS (S)[c]	–	–	–	–	$2.45 \cdot 10^{-2}$	0.546	0.9910
PS (S_h)[c]	–	–	–	–	$1.44 \cdot 10^{-2}$	0.561	0.9990

[a] Calculated from average log K. [b] Average of calculated K values. [c] Calculated from data taken from ref.[15]

RESULTS AND DISCUSSION

Measurements were made on samples of atactic, *cis,trans*-PPA (72% *cis*) similar to those used in our earlier study of PPA solutions by the SEC/LALS/Visco and other methods[6,9,14b]. Comparative analysis of almost stereoregular (*cis*-content > 95%) PPA samples prepared with various rhodium complexes[1d,1e] or dinuclear tungsten complexes[16] as catalysts could not be made because of easy *cis*-to-*trans* isomerization[1e,17a,17b] and aggregation[17c] of their molecules in solutions.

Scaling Law

Semilogarithmic molecular-weight distributions of studied PPA samples together with corresponding $\langle S^2 \rangle^{1/2} - M$ log–log plots of the radius-of-gyration scaling law

$$\langle S^2 \rangle^{1/2} = KM^{\sigma} \tag{3}$$

are shown in Fig. 1. Only data for fractions with $M > 150\,000$ were taken into consideration because the values of $\langle S^2 \rangle^{1/2}$ for smaller macromolecules suffer from higher experimental error. As can be seen, the scaling-law plots (each having correlation coefficient $r > 0.999$) are practically merged into a single straight line; the observed minute differences between particular plots are of the random type (see Table II). The determined values of the scaling law constants K and σ are summarized in Table II, in which also the values for polystyrene (PS) resulting from a critical evaluation of available literature data[15] are shown for comparison.

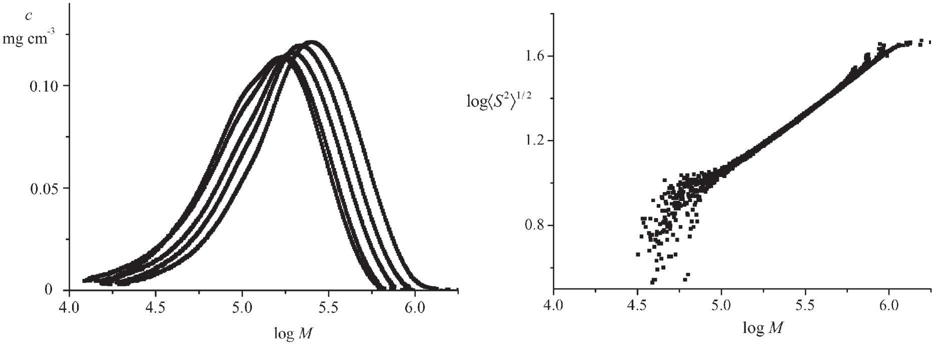


FIG. 1
Semilogarithmic molecular weight distributions (left) and scaling-law plots (right) of studied *cis,trans*-PPA samples; solvent THF, 25 °C

As can be seen, the values of the scaling-law constants K and σ found for PPA are close to those found for PS (saturated-main-chain analog of PPA) in the same solvent (THF). The scaling-law exponent σ is a function of the shape and rigidity of dissolved macromolecules. Theory[10,11] predicts $\sigma = 1/3$ for compact spherical molecules and $\sigma = 1$ for rod-like molecules; values from 0.5 to 0.6 are typical of random-coil macromolecules. Hence the obtained average value $\sigma = 0.584$ indicates the random-coil nature of PPA molecules in solution. Moreover, close values of K and σ for PPA and PS also explain our earlier observations[6] that the apparent molecular weight of *cis*,*trans*-PPA determined from SEC record on the basis of PS standards is close to that obtained by using the universal calibration approach.

Unperturbed Dimensions

The obtained pairs of M and $\langle S^2\rangle^{1/2}$ values were used to determine values of the unperturbed dimensions parameter $A_S = (\langle S^2\rangle_0/M)^{1/2}$ and the excluded volume parameter $B = \beta/M_\mathrm{u}^2$ of *cis*,*trans*-PPA. Here, M_u is the molecular weight of a monomeric unit and β is the effective volume excluded to one monomeric unit by the presence of another one and $A_S = 6^{1/2}A_R$ where $A_R = (\langle R^2\rangle_0/M)^{1/2}$ is the unperturbed dimensions parameter defined on the basis of $\langle R^2\rangle_0$. The determination was done using extrapolations according to equations derived from theoretical relations between the radius-of-gyration expansion factor $\alpha_S = (\langle S^2\rangle/\langle S^2\rangle_0)^{1/2}$ and the excluded volume parameter $z = (4\pi)^{-3/2}(B/A_S{}^3)M^{1/2}$, which were obtained under various approximations[10]. We have used the following five equations:

$$\left(\frac{\langle S^2\rangle}{M}\right)^{3/2} = A_S^3 + 1.914(4\pi)^{-3/2}BM^{1/2} \tag{4}$$

based on the Fixman[18] equation: $\alpha_S^3 = 1 + 1.914z$;

$$\frac{\langle S^2\rangle}{M} = A_S^2 + 1.276(4\pi)^{-3/2}BA_S^{-1}M^{1/2} \tag{5}$$

based on the Fixman[19] equation: $\alpha_S^2 = 1 + 1.276z$;

$$\frac{\langle S^2\rangle}{M} = 0.805A_S^2 + 0.8938(4\pi)^{-1}B^{2/3}M^{1/2} \tag{6}$$

based on the Ptitsyn[20] equation: $5.12\alpha_S^3 = 4.12 + (1 + 9.79z)^{2/3}$;

$$\frac{\langle S^2 \rangle}{M} = 0.541 A_S^2 + 0.1831 A_S^{0.62} B^{0.46} M^{0.23} \tag{7}$$

based on the Yamakawa–Tanaka[21] equation: $\alpha_S^2 = 0.541 + 0.459(1 + 6.04z)^{0.46}$; and

$$\frac{\langle S^2 \rangle}{M} = A_S^2 + 0.0286 B g(\alpha) \frac{M}{\langle S^2 \rangle^{1/2}} \tag{8}$$

based on the equation of Kurata, Stockmayer and Roig[22]: $\alpha_S^3 - \alpha_S = Czg(\alpha)$, where C is a constant (we used $C = 1.276$) and $g(\alpha)$ is a function of the expansion coefficient α (we used $g(\alpha) = 1$)[10].

Examples of plots according to Eqs (*4*) to (*8*) are shown in Fig. 2 and the determined values of parameters A_S and B obtained from these plots are given in Table III. As can be seen, all extrapolations gave similar values of both determined parameters except for extrapolations made according to Eq. (*7*), which, therefore, were not included in calculation of average values of parameters A_S and B. The found average value of $A_S = 300 \times 10^{-4}$ nm for atactic PPA is practically equal to that of atactic PS, the saturated analog of PPA (A_S values 280×10^{-4}–320×10^{-4} nm are reported for PS[23]). This value gives C_∞ ($C_\infty = 12 A_S^2 M_u/(s + d)^2$, where $M_u = 102.14$) in the interval from 13.2 to 14.0. The former value is obtained for $s = 0.154$ nm and $d = 0.135$ nm (lengths of non-conjugated single and double bonds) while the latter for $s = 0.143$ nm and $d = 0.138$ nm (bond lengths determined for unsubstituted poly(acetylene)s[8]). For comparison, $C_\infty \cong 11$ for PS[10,11,23] due to greater length of its main-chain bonds. More detailed analysis of the obtained results of obtained values A_S cannot be made since the mean-square end-to-end distance of unperturbed polyvinylene chains yet has not been calculated.

The observed equality of mean dimensions of PPA and PS molecules of the same molecular weight is somewhat surprising but it corresponds with conclusions drawn from viscometry measurements (see above). On the other hand, this observation strongly contradicts the assumed higher stiffness of conjugated chains, which should lead to higher dimensions of PPA molecules compared with the PS ones. This discrepancy suggests that there are one or more factors causing a decrease in dimensions of PPA chains in solution.

The simplest possible factor coming into consideration is slight branching of PPA chains, which, however, can be neither confirmed nor excluded on the basis of available knowledge. We can only declare that values of both the KMHS exponent α and the scaling-law exponent σ of PPA occur in the region typical of linear flexible polymers and that, within experimental errors, the exponent σ as well as parameters A_S and B of PPA do not change during the degradation of this polymer. These observations suggest absence

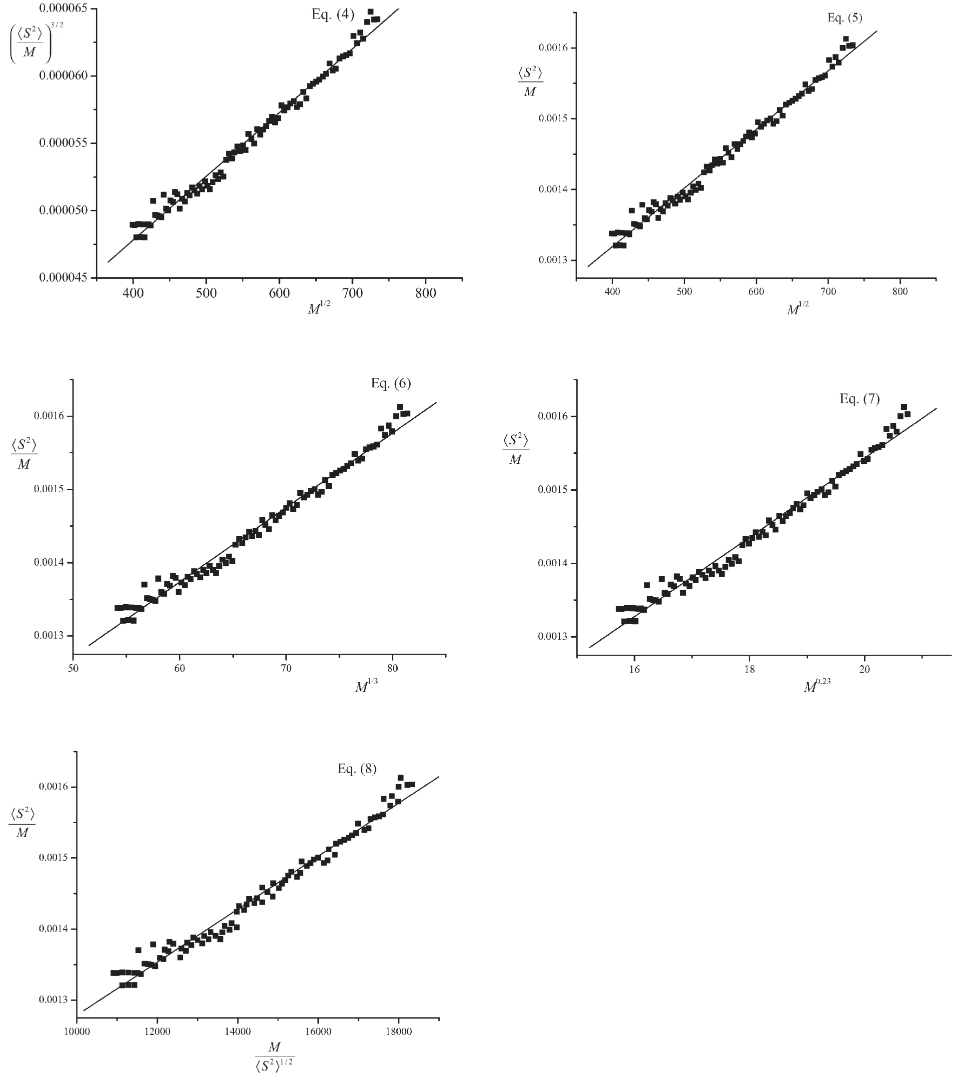


FIG. 2

Plots of extrapolations according to Eqs (*4*) to (*8*) for PPA sample C of branching of PPA molecules. On the other hand, rapidity of dissolving of PPA and other substituted polyvinylenes in various solvents indicates a very low to negligible entanglement of their molecules in a solid polymer, i.e., preference of intramolecular interactions over the intermolecular ones, which might be explained by branching of the molecules.

Enhanced attractive intramolecular interactions between high-polarizability PPA segments with delocalized π-electrons and the tendency of the segments to acquire near planar (cisoid, transoid) conformations provide an-

TABLE III
Values of unperturbed dimensions $A_S = (\langle S^2\rangle_0/M)^{1/2}$ and excluded volume parameter B of atactic PPA in THF obtained by extrapolations made according to the indicated equations; r is the correlation coefficient of particular extrapolation plot

PPA sample	Quantity	Eq.(*4*)	Eq.(*5*)	Eq.(*6*)	Eq.(*7*)[a]	Eq.(*8*)	Average[a]
A	A_S, 10^{-4} nm	300	310	296	*259*	292	300
	B, 10^{-6} nm^3	1.112	0.892	1.817	*3.391*	1.347	1.292
	r	0.997	0.998	0.996	*0.995*	0.995	0.996
B	A_S, 10^{-4} nm	302	300	280	*224*	278	290
	B, 10^{-6} nm^3	1.194	0.939	2.018	*4.718*	1.463	1.404
	r	0.994	0.995	0.993	*0.994*	0.991	0.993
C	A_S, 10^{-4} nm	306	314	309	*293*	301	308
	B, 10^{-6} nm^3	1.102	0.907	1.710	*2.465*	1.305	1.256
	r	0.993	0.994	0.992	*0.990*	0.989	0.991
D	A_S, 10^{-4} nm	279	291	271	*212*	270	278
	B, 10^{-6} nm^3	1.325	1.038	2.257	*5.555*	1.626	1.561
	r	0.991	0.991	0.989	*0.988*	0.985	0.988
E	A_S, 10^{-4} nm	325	330	317	*337*	322	324
	B, 10^{-6} nm^3	0.949	0.804	1.367	*1.632*	1.084	1.051
	r	0.968	0.969	0.966	*0.964*	0.955	0.963
Average	A_S, 10^{-4} nm	302	309	295	*262*	293	**300**[b]
	B, 10^{-6} nm^3	1.136	0.916	1.834	*3.552*	1.365	**1.313**
	r	0.989	0.989	0.987	*0.986*	0.983	**0.987**

[a] Data obtained using Eq. (*7*) are excluded. [b] This value gives the end-to-end unperturbed dimensions $A_R = 735 \times 10^{-4}$ nm.

other explanation of the above discrepancy. According to theoretical calculations, both single and double bonds are partially preserved in polyvinylene chains[1,8]. Also spectroscopic properties, particularly UV-VIS spectra clearly prove a limited extent of delocalization of π-electrons in polyvinylene chains[1–9]. This suggests that the PPA chain is composed of "oligomeric" straight segments of increased rigidity, in which π-electrons are well delocalized, and short folded segments with poorly delocalized π-electrons, acting as links between the straight segments. The segments with well-delocalized π-electrons should exhibit high polarizability giving them increased capability of non-covalent binding via attractive dispersion forces. It was shown that the π–π attraction forces between phenyl groups must be taken into account to calculate correct unperturbed dimensions of PS [24]. Accordingly, increased π–π attractive interactions between rigid segments can be regarded as an important factor compensating the influence of increased chain stiffness on dimensions of PPA molecules. The preference of near-planar conformations of main-chain single bonds together with the relatively high activation energy of conformational transitions should help to stabilize intramolecular associates of rigid segments. It is true that the similar mechanism, if operative, can produce interchain clusters of rigid segments, which should influence solution properties of the polymer. However, in this case mainly interactions between intramolecular clusters of different molecules come into consideration in dilute solutions, which can easily be destroyed by the Brownian-motion drift of macromolecules. Nevertheless, it should be mentioned here that a formation of organized, columnar supra-macromolecular structures has been observed in solid polymers of substituted acetylenes upon swelling or high-pressure treatment[25], however, only for the stereoregular (*cis*-transoid) polyvinylenes, association of which has been observed also in solutions[17c] (see above).

Summarizing the above discussion, the observed proximity of dilute solution characteristics of PPA and PS chains can be explained by increased π–π attraction forces between PPA segments with well-delocalized π-electrons, which compensate the effect of stiffening of these segments due to conjugation. Nevertheless, explanation based on a slight branching of PPA molecules cannot be excluded.

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