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Molecular characteristics of poly(1-trimethylsilyl-1-propyne) in dilute solutions

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Abstract

Samples and fractions of a membrane-forming polymer, poly(1-trimethylsilyl-1-propyne) (PTMSP), were studied by methods of molecular hydrodynamics (velocity sedimentation, translational isothermal diffusion and viscometry) in cyclohexane in the molecular mass range $60 < M \times 10^{-3}$ g mol$^{-1} < 430$. The following molecular-mass dependencies of the hydrodynamic characteristics (intrinsic viscosity $[\eta]$ (cm^3 g^{-1}), sedimentation coefficient $s_0(s)$ and translational diffusion coefficient D_0 (cm^2 s^{-1})) were established: $[\eta] = 0.198\, M^{0.50\pm0.06}$; $s_0 = 8.66 \times 10^{-16}\ M^{0.50\pm0.04}$; $D_0 = 9.30 \times 10^{-5}\ M^{-0.50\pm0.04}$. On the basis of the hydrodynamics data the equilibrium rigidity and hydrodynamic diameter of PTMSP chains were evaluated. The equilibrium properties of the different disubstituted polyacetylenes molecules are compared on the base of the normalised scaling plots.

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Keywords: Disubstituted polyacetylenes; Hydrodynamic properties; Macromolecular size

1. Introduction

Organosilicon polymers have long attracted attention as functional polymers [1,2]. Among them poly(1-trimethylsilyl-1-propyne) (PTMSP) is a polymer which forms a gas separating membrane with extraordinary high gas permeability and good selectivity. PTMSP exhibits also some other interesting properties. Some of its other applications are, for example, pervaporation in the separation of alcohol–water mixtures and the application as sensors and photoresistences [1]. Therefore, there is a great interest in the study of molecular and conformational characteristics of chains of disubstituted polyacetylens, in particular PTMSP.

PTMSP is obtained by catalytic polymerization from a low molecular mass acetylene derivative (1-trimethylsilyl-1-propyne) ($CH_3{-}C{\equiv}C{-}Si(CH_3)_3$) with halogenides of V, VI, VII group metals as catalysts [1,3]. However, the catalytic systems containing tantalum and niobium pentachlorides are mainly used in the synthesis. By using these catalysts by varying reaction temperature and type and concentrations of counterions, PTMSP can be obtained with molecular mass up to 10^6 with different ratios of *cis*- and *trans*-isomers. When the $NbCl_5$ catalyst is used *cis*-enriched samples with low molecular mass are obtained, whereas samples prepared on tantalum catalyst ($TaCl_5$), contain a greater fraction of *trans*-isomers and exhibit higher molecular mass. There are also the attempts to improve the membrane properties by synthesis of other disubstituted polyacetylenes or copolymers based on PTMSP [4,5].

Molecular characteristics of PTMSP obtained with different catalyst systems have been studied in many works [6–11]. Thus, in Refs. [6–8] hydrodynamic, dynamooptical and conformational properties of PTMSP synthesised by using $TaCl_5$/BuLi were investigated. In Ref. [10] mainly electrooptical properties of PTMSP obtained with different catalysts have been considered. It was shown that dynamooptical and electrooptical PTMSP properties are determined by type of catalyst systems with which this polymers were obtained [10]. However, it should be noted that there are contradictory evaluations in the literature about distribution type of stereoisomeric groups in PTMSP [10,11]. Hydrodynamic and conformational properties of PTMSP obtained with the $NbCl_5$ catalyst have been studied in Ref. [9]. However, the range of molecular mass determined by sedimentation–diffusion analysis is in this case only three-fold.

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In this work the samples and fractions of PTMSP obtained on $NbCl_5$ were studied in a wider range of molecular mass determined by the absolute method. This makes it possible to evaluate more reliably the equilibrium properties of PTMSP. Fundamental characteristics which should be determined in the study of any polymer are characteristics related to molecular mass and size of macromolecules in solutions. To obtain this information in this work, samples and fractions of membrane-forming polymer PTMSP obtained with $NbCl_5$ catalyst were studied by methods of molecular hydrodynamics (velocity sedimentation, translational isothermal diffusion and viscometry) and hydrodynamic characteristics of some disubstituted polyacetylenes were compared.

2. Experimental

PTMSP samples were synthesised by using $NbCl_5$ catalyst as has been described previously [12,13]. The average ratio of *cis–trans*-units according to ^{13}C NMR data are given in Table 1. One sample (9 in Table 1) was fractionated by fractional precipitation from solution in a toluene–CCl_4 mixture in 1:1 ratio. Ethanol was used as the precipitant and a number of fractions were obtained.

Hydrodynamic characteristics of samples and fractions were studied in solutions of cyclohexane. Cyclohexane at 25 °C has the following characteristics: viscosity $\eta_0 = 0.859 \times 10^{-2}$ mPa s, density $\rho_0 = 0.774$ g cm^{-3}.

Velocity sedimentation was investigated using an MOM 3180 analytical ultracentrifuge in a single-sector cell at a rotor revolution speed of 40×10^3 min^{-1}. A Lebedev polarising interferometer was used as the optical recording system [14]. Sedimentation coefficients, s(s), were calculated from the sedimentation boundary shift X, with time. The dependencies of $\Delta \ln X$ on Δt are show in Fig. 1a. These slopes give the values of $s = \omega^{-2}(\Delta \ln X/\Delta t)$, where $\omega = 2\pi n/60$ is the angular rotor revolution speed. The concentration dependence of sedimentation coefficient which satisfies a linear approximation $s^{-1} = s_0^{-1}(1 + k_s c + \cdots)$ was studied (Fig. 1b) for four samples (N 1, 3, 7, and 13 from Table 1). The solution concentration c is expressed in g cm^{-3}. The coefficients s_0 and k_s (cm^3 g^{-1}) were determined and following relationship was established between s_0 and k_s : $k_s = 11.7 s_0^{1.4\pm0.5}$ (s_0 in svedberg). This relationship was used for other fractions for the exclusion of the concentration effects on s_0 in the measurements of sedimentation coefficients at a single concentration.

Translational diffusion was studied in a Tsvetkov diffusometer [14] by the classical method of forming a boundary between the solution and the solvent, which was recorded using a polarising interferometer after definite time intervals. Diffusion interferogramms were processed by the method of maximum ordinate and area [14]. Diffusion coefficient $D = (1/2)(\Delta\sigma^2/\Delta t)$ was calculated from the slope of experimental dependence of dispersion σ^2 (cm^2) of diffusion boundary on experimental time (Fig. 2). The refractive index increments, $\Delta n/\Delta c$, were calculated from the area limited by the diffusion curve. The average value of $\Delta n/\Delta c$ is (0.16 ± 0.01) cm^3 g^{-1}.

Intrinsic viscosties, $[\eta]$ (cm^3 g^{-1}), were determined from the Huggins plots [14] $\eta_{sp}/c = [\eta] + k'[\eta]^2 c + \cdots$ (Fig. 3), were $\eta_{sp} \equiv (\eta - \eta_0)/\eta_0 = (t - t_0)/t_0$, η and η_0 are the viscosities of the solution and the solvent, t and t_0 are the times of solution and solvent flow in an Ostwald viscometer ($t_0 = 105.7$ s). The values of $[\eta]$ and Huggins parameter, k', and other hydrodynamic characteristics are given in Table 1. The average value of k' is (0.4 ± 0.1).

The buoyancy factor $(1 - \upsilon\rho_0)$ was determined from picnometric measurements by the slope of the dependence $\Delta m/m$ on w (Fig. 4) where w is the weight concentration, Δm is the difference between the weights of the solution (m) and

Table 1
Hydrodynamic and molecular characteristics of samples and fractions of PTMSP in cyclohexane at 25 °C

N	Isomer composition (*cis*/*trans*)	$[\eta]$ (cm^3 g^{-1})	K'	$D \times 10^7$ (cm^2 s^{-1})	$\Delta n/\Delta c$ (cm^3 g^{-1})	$s_0 \times 10^{13}$ (s)	$M_{sD} \times 10^{-3}$ (g mol^{-1})	$A_0 \times 10^{10}$ (g cm^2 c^{-2} deg^{-1} mol$^{-1/3}$)
1	70/30	151	0.11	1.49	0.148	6.05	429	3.74
2	60/40	100	0.38	1.78	0.159	4.9	298	3.48
3	60/40	91	0.44	1.87	0.154	4.75	274	3.45
4	80/20	82	0.52	2.14	0.173	4.7	237	3.57
5[a]		90	0.72	2.01	0.170	–	197[b]	–
6	60/40	79	0.49	2.24	0.163	3.95	190	3.49
7[a]		88	0.43	2.04	0.164	3.3	175	3.21
8[a]		100	0.44	1.95	0.167	3.1	172	3.12
9	60/40	91	0.45	2.15	0.154	–	159[b]	–
10	60/40	68	0.17	2.50	0.157	3.3	143	3.37
11[a]		74	0.44	2.71	0.200	2.55	101	3.35
12[a]		53	0.21	3.28	0.143	2.6	84	3.41
13[a]		50	0.54	3.58	0.169	2.2	67	3.38
14[a]		43	0.46	4.11	0.154	2.15	56	3.40

[a] Fractions of sample 9.

[b] $M_{\eta D}$.

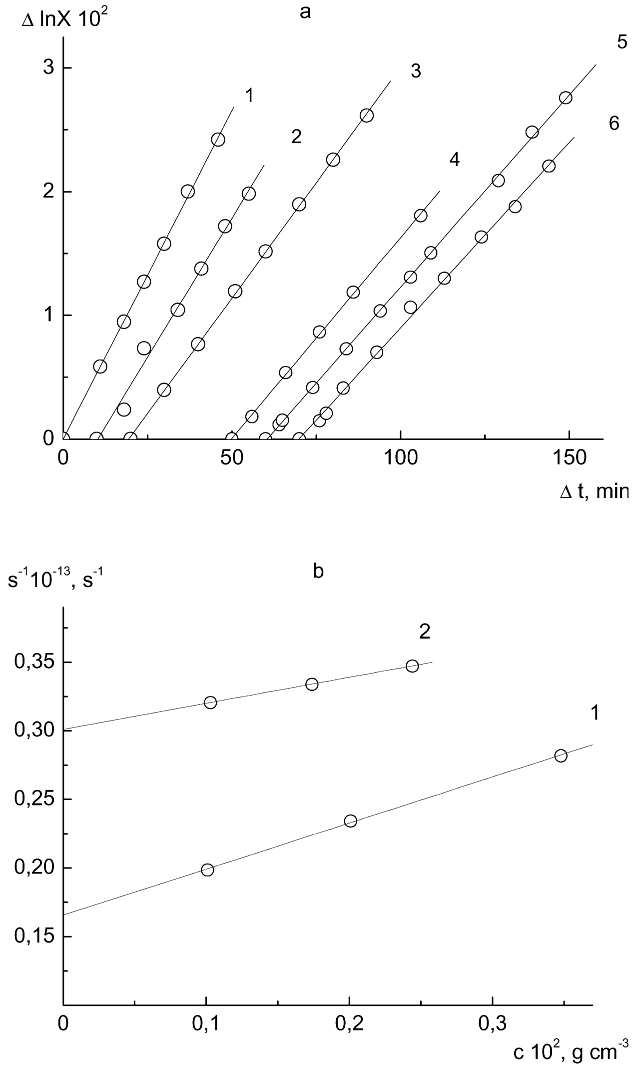

Fig. 1. (a) Dependencies of $\Delta \ln X$ on sedimentation time Δt, where X is the position of the sedimentation peak maximum for cyclohexane solutions of fractions 1 (1, 2, 3) and 7 (4, 5, 6) at concentrations $c \times 10^2$ g cm^{-3}, 0.101 (1); 0.201 (2); 0.348 (3); 0.103 (4); 0.174 (5); 0.244 (6). (b) The concentration dependence of s^{-1} for fractions 1 (1) and 11 (2).

the solvent (m_0) of equal volumes and $\Delta\rho$ is the corresponding difference between the density of the solution (ρ) and the density of the solvent (ρ_0). The data shown in Fig. 4 give: $\Delta m/wm = \Delta\rho/w\rho = \Delta\rho/c = (1 - \upsilon\rho_0) = 0.230 \pm 0.008$, what corresponds to the specific partial volume value $\upsilon = (0.995 \pm 0.010)$ cm^3 g^{-1}.

3. Discussion of results

On the basis of the hydrodynamics characteristics given in Table 1, the following values were calculated: molecular mass according to Svedberg [14], the hydrodynamic invariant, A_0 [14], and the sedimentation parameter β_s [15] according to the equations:

$$M_{SD} = R[s]/[D] \tag{1}$$

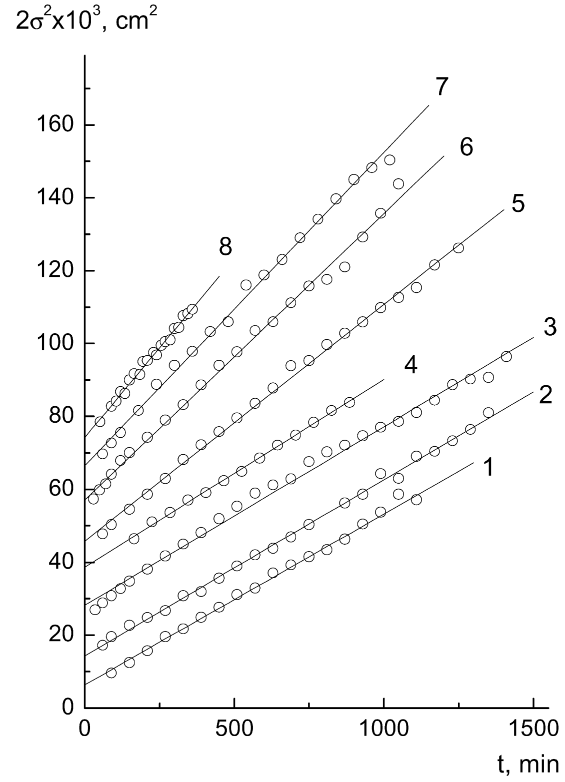

Fig. 2. Dependence of the diffusion dispersion $2\sigma^2$ vs. time of diffusion t. The figures correspond to the figures of Table 1: 1–8, 2–5, 3–7, 4–9, 5–11, 6–12, 7–13, 8–14.

$$A_0 = (R[D]^2[s][\eta])^{1/3} \tag{2}$$

$$\beta_s = N_A(R^{-2}[D]^2[s]k_s)^{1/3} \tag{3}$$

where $[s] \equiv s_0\eta_0/(1 - \upsilon\rho_0)$, $[D] \equiv D_0\eta_0/T$, R is the universal gas constant, N_A is the Avogadro number, and T is the temperature in degrees Kelvin.

The molecular mass and hydrodynamic invariants for PTMSP are listed in Table 1. The mean value of hydrodynamic invariant is $A_0 = (3.4 \pm 0.15) \times 10^{-10}$ g cm^2 c^{-2} deg^{-1} mol$^{-1/3}$, and the average value of the sedimentation parameter is $\beta_s = (1.1 \pm 0.15) \times 10^7$ mol$^{-1/3}$. These values are characteristics of linear polymer homologues [14,15] The mean value of hydrodynamic invariant A_0 were used for calculating the molecular mass of sample 5 and 9 (Table 1) from the following equation:

$$M_{D\eta} = 100A_0^3([D]^3[\eta])^{-1} \tag{4}$$

Fig. 5 gives in a double logarithmic scale the molecular-mass dependencies of characteristics hydrodynamic values $[\eta]$, $[s]$ and $[D]$ for PTMSP samples and fractions in cyclohexane. Taking into account the errors in numerical coefficients determination, these dependencies can be approximated by the following equations:

$$[\eta] = 0.198M^{0.50 \pm 0.06} \tag{5}$$

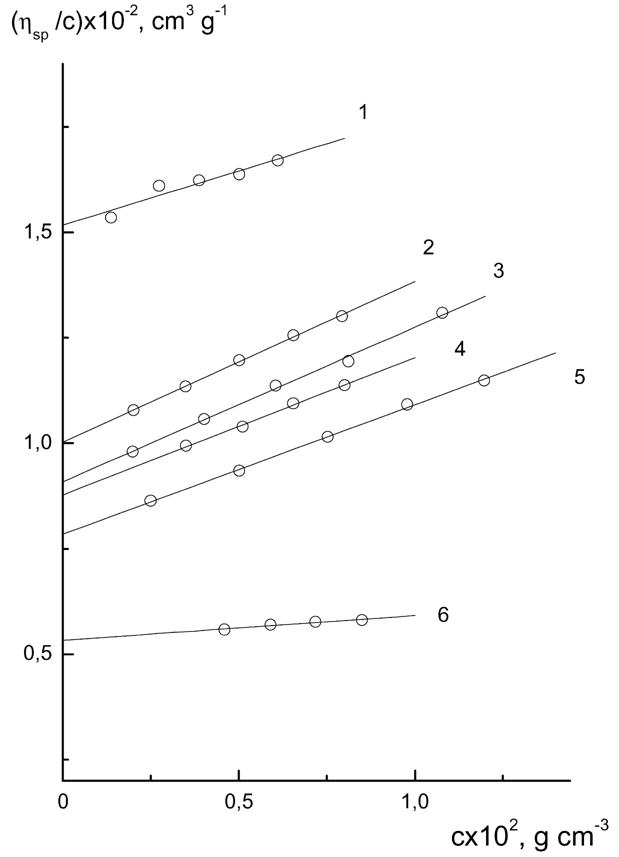

Fig. 3. Dependence of η_{sp}/c vs. concentration c. The figures correspond to the figures of Table 1: 1–1, 2–2, 3–3, 4–7, 5–6, 6–12.

$$s_0 = 8.66\times10^{-16}M^{0.50\pm0.04} \quad (6)$$

$$D_0 = 9.30\times10^{-5}M^{-0.50\pm0.04} \quad (7)$$

If the following relationship between scaling indexes b_η and $|b_D|$ (or b_s; $|b_D| + b_s \equiv 1$): $|b_D| = 1/3(b_\eta + 1)$ is strictly fulfilled. It is possibly to evaluate from pre-exponential K_η and K_D (or K_S) the average value of hydrodynamic invariant A_0 can be evaluated from the equations:

$$K_\eta^{1/3}K_D = A_0(T/\eta_0) \quad (8)$$

$$K_\eta^{1/3}K_S = A_0[(1-\upsilon\rho_0)/(R\eta_0)] \quad (9)$$

It is easy to see that it corresponds to the mean arithmetic value of A_0 obtained from the data in Table 1.

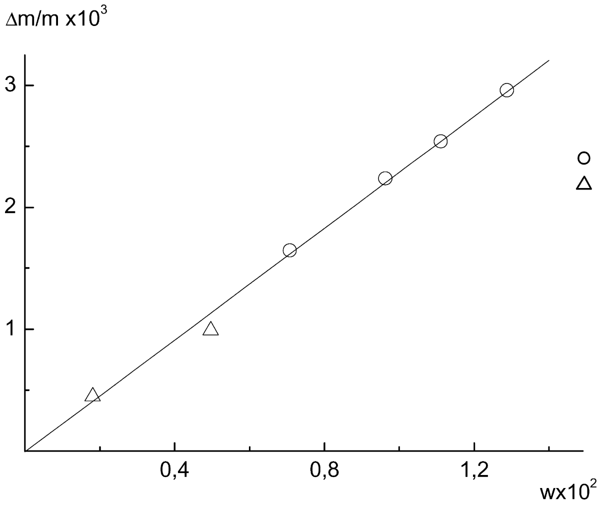

Fig. 4. Determination of the buoyancy factor $(1-\upsilon\rho_0) \equiv \Delta m/wm$, where $\Delta m = m - m_0$, and m and m_0 are the mass of the same volume of solution and solvent, respectively, w is the weight concentration of the solution. The figures correspond to the figures of Table 1: 1–9, 2–3.

Fig. 5 shows also the comparison of results in Ref. [9] $[\eta]$ being measured in toluene, and s and D in chloroform. It is clear that the system of points corresponding to Ref. [9] is only slightly shifted with respect to the results obtained in cyclohexane.

This slight shift may be probably due to the difference in thermodynamic quality of the solvents compared because both toluene and chloroform are thermodynamically ‘poorer’ solvents for PTMSP than cyclohexane.

4. Evaluation of equilibrium rigidity of PTMSP chains

Since the value of scaling indexed $a = 0.5$ is a good approximation, this means that the behaviour of PTMSP chains corresponds to that of relatively long linear chains (i.e. Gaussian chains) which the influence of excluded volume effects is a not manifested. In this case it is possible to evaluate the equilibrium rigidity (segment Kuhn length or persistence length) by using the theories describing the hydrodynamic behaviour of a wormlike necklace (Hearst–Stockmayer theory [16]) and wormlike cylinder (Yamakawa–Fujii theory [17]) without volume interactions. In this case the following equation is used for translational friction data:

$$[s]P_0N_A = (M_L/A)^{1/2}M^{1/2} + (M_LP_0/3\pi)[\ln(A/d) - \varphi(0)] \quad (10)$$

where M_L is the molecular mass of unit chain length, d is the chain hydrodynamic diameter, P_0 is the Flory parameter, $\varphi(0) = 1.431$ [16], $\varphi(0) = 1.056$ [17].

To interpret viscometric data Bushin–Tsvetkov's plot [14] is used:

$$(M^2\Phi_0/[\eta])^{1/3} = (M_L/A)^{1/2}M^{1/2} + (M_LP_0/3\pi)[\ln(A/d) - \varphi(0)] \quad (11)$$

where Φ_0, and P_0 are the Flory parameters.

To evaluate the equilibrium rigidity and hydrodynamic diameter from dependencies (Eqs. (10) and (11)) shown in Fig. 6, it is necessary to determine the value of $M_L = M_0/\lambda$, where $M_0 = 112$ is the molecular mass of the monomer unit and λ is the length of its projection on the chain direction.

Experimental values of λ obtained from crystallographic data for polyacetylenes are reported in the literature. For the so-called *cis*-polyacetylene $2\lambda = 4.38\times10^{-8}$ cm [18] and

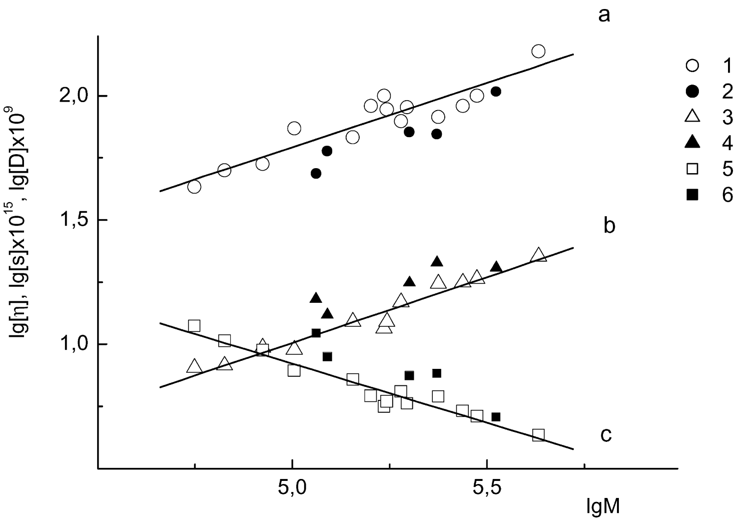

Fig. 5. Kuhn–Mark–Houwink–Sakurada plots: (a) [η], (b) [s], (c) [D]. The data 1, 3 and 5 correspond to the data of Table 1; the data 2, 4 and 6 correspond to the data presented in Ref. [9].

$2\lambda = 4.47 \times 10^{-8}$ cm [19,20], the average value is correspondingly equal to $\lambda = 2.22 \times 10^{-8}$ cm. In this case the *cis*-transoid and *trans*-cisoid (virtually equivalent to it) chain conformations are really considered. The isomer composition of the chain in this case is 50:50. For completely *trans*-polyacetylene, the value $\lambda_{trans} = 2.46 \times 10^{-8}$ cm was obtained according to the data of electronic diffraction of fibrils completely isomerized into the *trans*-form at 200 °C [21]. Assuming to the first approximation the additivity of λ in the bonding of *cis*- and *trans*-isomers into a single chain, we will evaluate λ for completely *cis*-isomer of polyacetylene as $\lambda_{cis} = 1.98 \times 10^{-8}$ cm. In the additive approximation for polyacetylene with the 60:40 composition, the average length of repeat unit projection on chain direction will be $\lambda = 1.98 \times 0.6 + 2.46 \times 0.4 = 2.17(\times 10^{-8}$ cm).

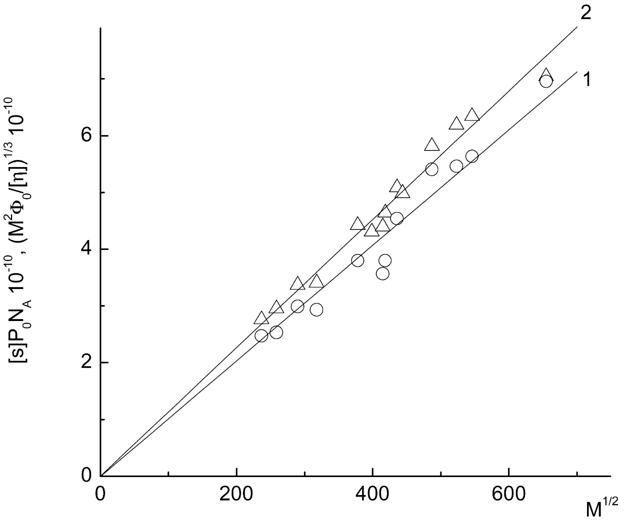

Fig. 6. Plots of $[s]P_0N_A$ (1) and $(M^2\Phi_0/[\eta])^{1/3}$ (2) vs. $M^{1/2}$ for PTMSP molecules in cyclohexane.

On the other hand, the value of λ can also be evaluated from the results of quantum–chemical calculation of decamer fragments of PTMSP chains [10]. Helical conformations were found to be the most energetically advantageous for these fragments. Moreover, for the *cis*-decamer it is a 3_1-helix (the helix pitch is formed of three monomer units) and for *trans*-decamer it is the 4_1-helix. The pitch of the *cis*-helix was found to be 5.4×10^{-8} cm and that of the *trans*-helix was 9.3×10^{-8} cm. This corresponds to the length of the repeat unit in main chain direction $\lambda_{cis} = 1.8 \times 10^{-8}$ cm and $\lambda_{trans} = 2.3 \times 10^{-8}$ cm. On the basis of these values the additive value of λ is 2.0×10^{-8} cm, which is in relatively good agreement with the value obtained from crystallographic data.

The above values of λ will be used from calculating the Kuhn segment length for PTMSP chains studied by us. The average value of the Kuhn segment length was obtained from viscometric data at the theoretical value of the Flory parameter $\Phi_0 = 2.87 \times 10^{23}$ mol^{-1} [16] $A_\eta = 42 \times 10^{-8}$ cm. From data on translational friction at $P_0 = 5.11$ [16] it follows that $A_f = 54 \times 10^{-8}$ cm.

The average value of A, $A = (48 \pm 6) \times 10^{-8}$ cm, will be taken as the value of the Kuhn segment length of PTMSP chains. The evaluation of the diameter of the chain simulating the macromolecule depends on the character of the hydrodynamic model. In the case of a persistent necklace [16], the equality to zero of the member describing draining means that the ratio $A/d \approx 4.2$ at using the model of solid persistent cylinder the theory [19,20] leads to $A/d \approx 2.9$. Hence, we obtain as the average value of hydrodynamic diameter d equal to $(14 \pm 3) \times 10^{-8}$ cm. This value is in good agreement with $d = 11 \times 10^{-8}$ cm obtained from crystallographic studies of polyacetylene [18].

Consequently in the range of molecular mass $60 \times < M \times 10^{-3}\ g\ mol^{-1} < 430$ scaling relationships were obtained for hydrodynamic characteristics of PTMSP molecules in cyclohexane and equilibrium rigidity of its chains was evaluated.

5. Comparison of hydrodynamic behaviour of disubstituted polyacetylenes

The values characterising the equilibrium rigidity of different disubstituted polyacetylenes studied up to the present were compared [6,7,9,22–24].

As compared with other methods the intrinsic viscosity was studied for a greater number of systems. This makes it possible to compare a wider number of experimental results.

Let us compare the results obtained in interpreting values of intrinsic viscosity in combination with those of molecular mass obtained by one absolute method: light scattering, or sedimentation–diffusion analysis. The following systems will be discussed: PTMSP ($NbCl_5$) [8], PTMSP ($TaCl_5$) [6, 7], poly(1-trimethylgermyl-1-propyne)($TaCl_5$) [23], poly(1-phenyl-1-propyne) ($TaCl_5$) [22], poly(1-phenyl-1-butyne) ($TaCl_5$) [24], poly(1-phenyl-1-nonyne) ($TaCl_5$) [24]. In the study of PTMSP molecules, some objective difficulties exist leading to ambiguous interpretation of experimental results in the framework of concepts of a homogeneous linear homopolymer chain. First, in samples of disubstituted polyacetylenes some not strictly distributed quantity of *cis*- and *trans*-units is always present. Second, narrow molecular-mass range is observed as a rule for samples obtained with a single catalyst system.

Table 2 gives the molecular mass ranges of the investigated polymers. It can be seen that in most cases this range is very narrow. This may lead to considerable errors in the determination of A and, in particular, in that of hydrodynamic diameter d. Among disubstituted polyacetylenes only one system covers approximately a 100-fold MW molecular mass range. This is poly(1-phenyl-1-propyne) (PPP) [22], which differs from poly(α-methylstyrene) only by presence of one double bond in the repeating unit. It is known that cyclohexane is a θ-solvent at 35–36 °C for poly(α-methylstyrene) [25]. Therefore, in Ref. [22] cyclohexane at 36 °C was used as the basic solvent for evaluating the equilibrium rigidity of PPP-chains. The authors detected a tendency of increasing the slope with the decreasing molecular mass in double logarithmic dependence of $[\eta]$ in cyclohexane on molecular mass M_W. This suggested that for this polymer–solvent system intramolecular excluded volume effects could be neglected and the data can be interpreted from the stand-point of theories taking into account intramolecular draining effects. Nevertheless, for the same fractions studied in toluene at high molecular mass, greater values of $[\eta]$ were obtained than in cyclohexane. The change of the slope does not observed in the case of toluene solutions. This may indicate different thermodynamis qualities of the solvents being compared and the existence of excluded volume effects in poly(1-phenyl-1-propyne) chains in toluene. This means that polymers of disubstituted acetylenes belong to a class of semirigid macromolecules. For these molecules both the excluded volume effects and intramolecular draining can be manifested, which additionally hinders the interpretation of results. The possibility of manifestation of these two effects depends on the range of investigated molecular mass of the corresponding polymers.

Therefore, to interpret the above cited data, a relationship was used obtained on the basis of the Gray–Bloomfeld–Hearst theory [26,27]. This equation considers the dependence of translational friction coefficient of a wormlike necklace on molecular mass taking into account the influence of intramolecular excluded volume effects on chain size. The subsequent replacement of variables according to the equation [27,28]:

$$[s]P_0N_A = (M^2\Phi_0/[\eta])^{1/3} \tag{12}$$

makes it possible to interpret viscometric data over the entire molecular mass range by using the following equation:

$$\begin{aligned}(M^2\Phi_0/[\eta])^{1/3} &= [3/(1-\varepsilon)(3-\varepsilon)]M_L^{(1+\varepsilon)/2}A^{-(1-\varepsilon)/2}M^{(1-\varepsilon)/2} \\ &\quad + (M_LP_0/3\pi)[\ln(A/d) - \varphi(\varepsilon)]\end{aligned} \tag{13}$$

Table 2
Equilibrium rigidity of disubstituted polyacetylenes $[-CR_1{=}CR_2-]_n$ according to the viscometric results

R_1; R_2	Isomer composition (*cis/trans*)	Catalyst	M_0 (g mol^{-1})	Solvent	Interval of $M \times 10^{-5}$	b_η	A_η[b] × 10^8 cm	References
$Si(CH_3)_3$; CH_3	65/35	$NbCl_5$	112	Toluene	1.2–3.3	0.59	44 ± 5	[9]
$Si(CH_3)_3$; CH_3	60/40	$NbCl_5$	112	Cyclohexane	0.6–4.3	0.50	42 ± 5	Table 1
$Si(CH_3)_3$; CH_3	40/60	$TaCl_5$/BuLi	112	Heptane	3–33	0.83	65 ± 4	[7]
$Si(CH_3)_3$; CH_3	[a]	$TaCl_5$	112	Toluene	2.5–9	0.88	62 ± 15	[6]
$Ge(CH_3)_3$; CH_3	10/90	$TaCl_5$/BuLi	157	Cyclohexane	5–17	0.71	64 ± 12	[23]
C_6H_5; CH_3	[a]	$TaCl_5$	116	Cyclohexane	0.15–14.5	0.65	63 ± 1	[22]
C_6H_5; CH_3	[a]	$TaCl_5$	116	Toluene	0.15–14.5	0.75	63 ± 1	[22]
C_6H_5; C_2H_5	[a]	$NbCl_5$; $NbBr_5$; $TaBr_5$	130	Toluene	0.5–2.6	0.91	160 ± 30	[24]
C_6H_5; C_7H_{15}	[a]	$NbCl_5$; $NbBr_5$; $TaBr_5$	200	Toluene	0.2–1.2	1.06	200 ± 50	[24]

[a] Isomer composition is not indicated in original works.

[b] For all systems the values A_η were calculated using the relationship (13) with the value of $\Phi_0 = 2.87 \times 10^{23}$ mol^{-1}

where ε is the parameter characterising the thermodynamic quality of the solvent [29] and $\varphi(\varepsilon) = 1.431 + 2.635\varepsilon + 4.709\varepsilon^2$ [27]. The upper limit of the parameter ε can be evaluated from the equation: $\varepsilon = (2b_\eta - 1)/3$. Its lower limit is the value $\varepsilon = 0$ corresponding to the absence of intrachain excluded volume effects. Hence, by using Eq. (13), data were processed for all investigated disubstituted polyacetylenes. Table 2 gives the results from which the following conclusions can be made. The equilibrium rigidity of PTMSP molecules obtained with $TaCl_5$ is 1.5 times greater than that of PTMSP molecules obtained with $NbCl_5$. This is due to a greater fraction of *cis*-isomers in PTMSP chain obtained with $NbCl_5$ leading to a greater coiling of macromolecules. The replacement of a silicon atom ($M_{Si} = 28.1\ \mathrm{g\ mol^{-1}}$) by a germanium one ($M_{Ge} = 72.6\ \mathrm{g\ mol^{-1}}$) does not lead to a change in equilibrium rigidity, just as the replacement $Si(CH_3)_3$ group by the phenyl group. The greatest increase in equilibrium rigidity is observed in samples which contain in the repeat unit aliphatic groups longer that CH_3 ($-C_2H_5$ and $-C_7H_{15}$). It is interesting to note that for polyalkylacrylates and polyalkylmethacrylates [30,31] such increase in side group length is not accompanied by any marked increase in equilibrium rigidity. In the case of disubstituted polyacetylenes, the inclusion of a side aliphatic group (as well as the presence of phenyl rings in the side chain) probably on the one hand causes the degeneration of *cis*-isomers (although the samples were also obtained on Nb catalyst) because by great steric limitations introduced by bulky aliphatic groups. On the other hand, conjugated portions in the main chains probably become longer. All this leads to a considerable increase in the equilibrium rigidity of the poly(1-phenyl-1-butyne) and poly(1-phenyl-1-nonyne) chains. The results for different disubstituted polyacetylenes can be compared to using the concept of normalised scaling [32]. The dependence of $\log[\eta]$ on $\log M$ (Fig. 7a) can be represented in a system of coordinates: $\log([\eta]M_L) - \log(M/M_L)$ (Fig. 7b), which take into account the change in the repeat unit mass for different polymers. This dependence ($[\eta]M_L - M/M_L$) makes it possible to range linear polymers according to coil sizes. The points located higher on the $[\eta]\ M_L$ axis refer to chains occupying a greater volume in solution at the same degree of polymerization. The evaluation of equilibrium rigidity gives the coordinates $\log([\eta]M_L A^{-2}) - \log(M/M_L A^{-1})$ (Fig. 7c), which make it possible to reduce all the systems considered virtually to a single curve. This means that in interpreting the hydrodynamic values for linear disubstituted polyacetylenes these molecules can be simulated by linear chains, the main characteristics of which are equilibrium rigidity values and unit length mass (M_L).

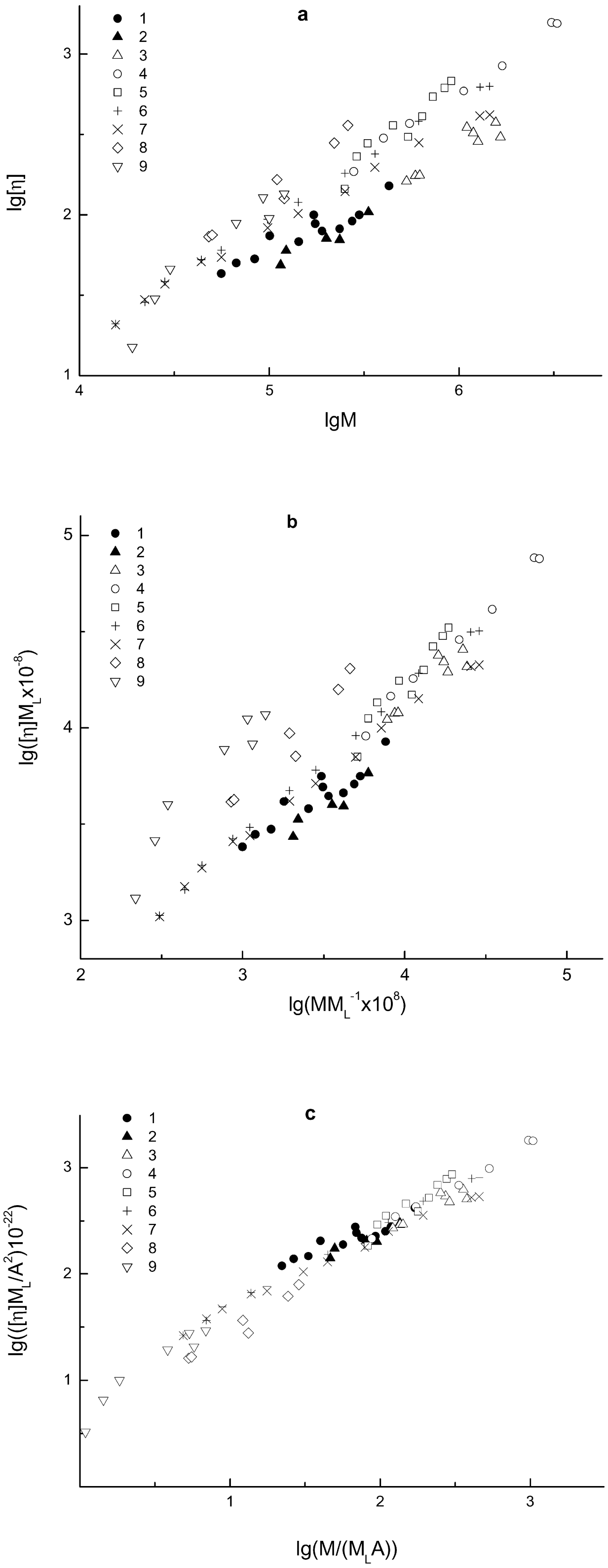

Fig. 7. Scaling plots to compare the different disubstituted polyacetylenes molecules: (a) common Kuhn–Mark–Houwink–Sakurada plot; (b) one time normalized scaling plot with the value of M_L : ($[\eta]M_L$) vs. M/M_L; (c) double normalized plot: ($[\eta]M_L/A^2$) vs. $M/(M_L A)$. The data are from: (1) Table 1, (2) [9], (3) [23], (4) [7], (5) [6], (6,7) [22], (8,9) [24].

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