Investigation of Macromolecules Exhibiting the Structure of a Once-Broken Rod by Molecular Optics. 1. Synthesis and Investigation of Poly(γ-benzyl L-glutamate) with Short Joints

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ABSTRACT: Samples of poly(γ-benzyl L-glutamate) (PBG) have been synthesized. Their chain contains one of the following fragments: a bis(*o*-(glycylamino)phenyl) disulfide, an azobisisobutyrohydrazide, or a decamethylenediamine fragment. These macromolecules were considered to have the shape of a once-broken rod. Solutions of the synthesized samples were investigated in dimethylformamide (DMF) at 25 °C by light scattering, flow birefringence (FB), and viscometry. For comparison, similar investigations were carried out for PBG over a wide molecular weight range. Equations were obtained relating intrinsic viscosity to molecular weight for all the investigated structures. The mean-square size of the macromolecules, the second virial coefficients, and the shear optical coefficients were determined. The value of the effective persistence length a was determined for all structures from the experimental data on intrinsic viscosity and FB. It was shown that only the introduction of the decamethylene fragment into the PBG chain decreases the equilibrium rigidity (by 25–30%).

Introduction

The aim of the present paper was to investigate the effect of groups of various chemical nature introduced into the poly(γ-benzyl L-glutamate) (PBG) chain on the conformational characteristics of its macromolecules. The insertion of a joint makes it possible to consider the PBG molecule as a once-broken rod.

The problem of the effect of one break in the macromolecule on its rigidity has been considered theoretically and investigated experimentally in a number of papers.[1–7] The opinions of the authors of the above papers on this problem differ, and therefore a thorough and comprehensive study of the conformational properties of PBG containing short joints in the chain in dilute solutions is topical and interesting.

Three types of modified PBG structures were obtained and fractionated. They contain one of the chain fragments shown in Chart I.

It is determined by the conditions of the synthesis[8,9] that all the investigated modified PBG structures contain only one joint in the chain. PBG samples for comparative investigation have been synthesized according to ref 10 and fractionated.

Experimental Section

The *N*-carboxyanhydride (*N*-CA) of γ-benzyl L-glutamate was obtained by Fuller's method. Initiators, *o*-DGADPDS and ABIH, were synthesized by published methods, refs 12 and 13, respectively. Decamethylenediamine was dried under vacuum over KOH and then distilled under vacuum (T_{boil} = 140 °C/12 mmHg).

Polymerization. A 3% *N*-CA solution in dioxane was polymerized with *o*-DGADPDS or ABIH in an anhydride/initiator ratio (A/I) from 40 to 300. A 2% solution of *N*-CA in dioxane was polymerized with decamethylenediamine in an A/I ratio of 100, 500, and 1000. All polymers were precipitated from dioxane into methanol. Conversion was 75–99%. Some samples were fractionated by precipitation from chloroform into methanol. It should be borne in mind that the samples could contain a certain amount of the PBG homopolymer because simultaneous *N*-CA polymerization could proceed both by the "primary amine" mechanism (i.e., with the inclusion of an initiator fragment into the chain) and by the "activated monomer" mechanism.[14] It cannot be ruled out that molecules having the shape of once-broken rod are partially inhomogeneous with respect to molecular weight and the location of the joint in the chain.

Solutions of the samples and fractions in DMF were investigated by light scattering, FB, and viscometry at 25 °C. DMF of "chemically pure" grade was dried over calcium hydride for 2 days and distilled under vacuum over ninhydrin in order to remove traces of amines.

The intrinsic viscosity $[\eta]$ of the samples was measured in an Ostwald capillary viscometer corresponding to the rate gradient range $g \sim 300\ s^{-1}$. For solutions of the samples with the highest molecular weights (nos. 10–12 in Table I), values of $[\eta]$ were obtained at low rate gradients (g = 0.4–1.1 s^{-1}) to determine the dependence of viscosity on shear stress. A modified Zimm rotational viscometer[15] was used to measure $[\eta]$ at low g values. Comparison of the values of $[\eta]$ obtained for samples 10–12 at $g \sim 300\ s^{-1}$ and g = 0.4–1.1 s^{-1} gave the following results. For sample 12 the value of $[\eta]$ at g = 0.4–1.1 s^{-1} exceeded those at $g \sim 300\ s^{-1}$ by 25%. For sample 11 this increase was only 10%, and for sample 10 a dependence of viscosity on shear stress was not observed at all. Values of $[\eta]$ for samples 11 and 12 extrapolated to $g = 0$ are given in Table I. Values of the Huggins constants k' were 0.4–0.6.

Light scattering was measured by a standard procedure[16] with a Sofica photogoniodiffusometer at a wavelength of 546 nm in the concentration range C = (0.05–1.5) × 10^{-2} g/cm^3, and calibration was carried out against benzene (R_v = 2.32 × 10^{-5} cm^{-1}). Dust was removed from solutions by centrifugation at 15 000 rev/min for 1 h. The results were processed by the Debye method (from scattering asymmetry $[Z]$).[16] For sample 12b (Table I) the Zimm plot was also obtained (Figure 1). The difference in the values of the weight-average molecular weight M_w in the processing of results obtained according to Debye and Zimm was 10%. Refractive index increments were measured with an IRF-23 refractometer (USSR) with a differential cell. The value of dn/dc averaged for all samples was 0.110.

FB was measured visually by a standard method[17] in a titanium dynamooptimeter with a gap width of 0.03 cm and a rotor height of 3 cm. The range of velocity gradient g was 50–3000 s^{-1}. The value of FB was positive in sign and varied proportionally to g. The value of the intrinsic orientation angle $[\chi/g]$ was obtained by extrapolating the orientation angle to zero velocity gradient and zero concentration. The shear optical coefficient $\Delta n/\Delta\tau = \Delta n/[g(\eta - \eta_0)]$ (η and η_0 are the viscosities of the solution and the solvent, respectively) is independent of polymer concentration

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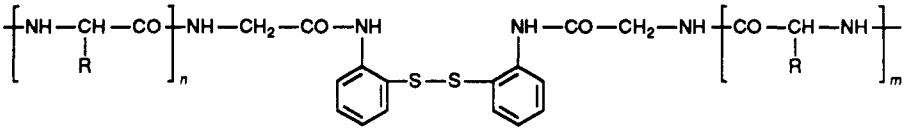
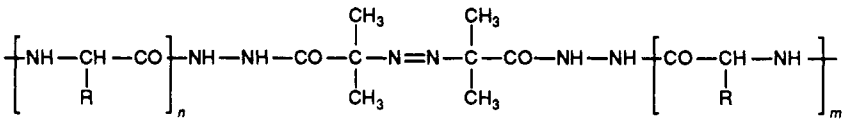
Chart I[a]

1. 2,2′-Bis(diglycylaminophenyl) disulfide (o-DGADPDS)



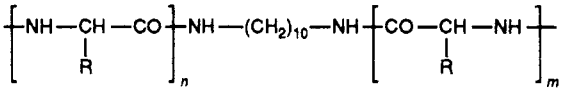
PBG–S–S–PBG

2. 2,2′-Azobisisobutyrohydrazide (ABIH)



PBG–N=N–PBG

3. Decamethylenediamine



PBG–$(CH_2)_{10}$–PBG

[a] R is $(CH_2)_2COOCHC_6H_5$.

Table I
Molecular Characteristics of PBG Samples in DMF at 25 °C

sample no.	$[\eta] \times 10^{-2}$, cm^3/g	$M_w \times 10^{-3}$	$A_2 \times 10^4$, $cm^3/(g^2\ mol)$	$\langle h^2 \rangle^{1/2} \times 10^8$, cm	$\langle h^2 \rangle / M \times 10^{16}$, cm^2	$(\Delta\eta/\Delta\tau) \times 10^{10}$, $(cm\ s^2)/g$
1	0.37	55	3.3			320
2	0.53	80	2.7			400
3 fr	0.65	80	2.9			370
4 fr	1.70	170	1.8	1100	7.1	600
5 fr	2.20	210	2.3	1200	6.9	700
6 fr	4.00	360[a]				850
7	6.00	350	2.8	1900	10.3	1000
8 fr	8.50	500[a]				950
9 fr	10.80	600[a]				1000
10 fr	12.80	630	2.5	2600	10.7	1200
11 fr	18.30	790	1.8	2900	10.7	1200
12[b]						
a fr	30.00	1100	1.7	3500	11.1	1500
b fr	30.00	1100	1.1	3500	11.1	1500

[a] The value of M was determined from the equation $M = [\chi/g]RT/G\eta_0[\eta]$,[17] where $[\chi/g]$ is the experimental value of the intrinsic orientation angle of FB; the parameter $G = 0.6$. [b] For sample 12 the characteristics of the two fractions a and b are given. The complete coincidence between the values of the molecular parameters shows that this sample is monodisperse.

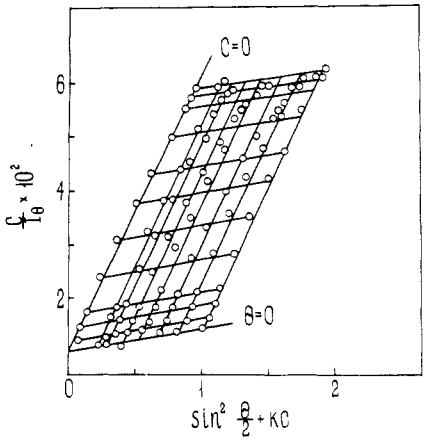


Figure 1. Zimm plot for sample 12b in DMF.

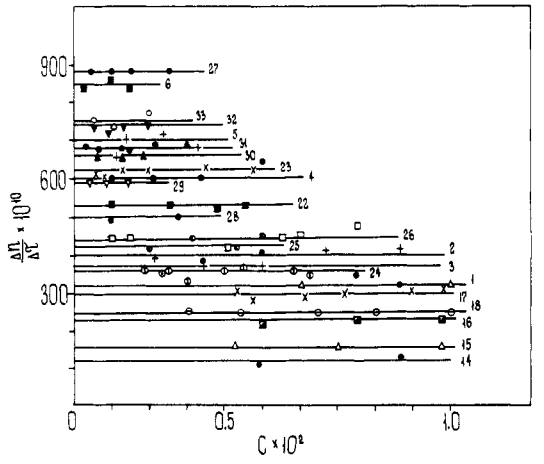


Figure 2. Concentration dependence of shear optical coefficient $\Delta n/\Delta\tau$ for samples of PBG (1–6), PBG–S–S–PBG (14–18, 22, 23), PBG–N=N–PBG (24–27), and PBG–$(CH_2)_{10}$–PBG (28–33) in DMF. Figures at the curves are sample and fraction numbers in Tables I and II.

(Figure 2). The values of $(\Delta n/\Delta\tau)_{c\to 0,g\to 0}$ obtained here are given in Tables I and II. For high molecular weight PBG samples (samples 7–12), the value of η for the investigated concentrations differs little from η_0. Hence, the value of intrinsic FB, $[n]$, was determined at these concentrations by extrapolating the experimental values of $\Delta n/gc\eta_0$ to the zero value of gradient and to zero concentration (Figure 3). In this case the shear optical coefficient was found from the $[n]/[\eta]$ ratio.

Results and Discussion

Light Scattering and Viscosity. Tables I and II give the values of M_w, $[\eta]$, the second virial coefficients A_2, and

Table II
Molecular Characteristics of PBG Samples Containing Groups of Various Nature in DMF at 25 °C

sample no.	$[\eta] \times 10^{-2}$, cm^3/g	$M_w \times 10^{-3}$	$A_2 \times 10^4$, $cm^3/(g^2\ mol)$	$\langle h^2\rangle^{1/2} \times 10^8$, cm	$\langle h^2\rangle/M \times 10^{16}$, cm^2	$(\Delta\eta/\Delta\tau) \times 10^{10}$, $(cm\ s^2)/g$
			PBG–S–S–PBG			
13	0.05	4	13.7			
14	0.15	30	4.6			120
15	0.20	40	3.1			160
16	0.28	50	3.4			230
17	0.28	55	3.8			300
18	0.38	60	3.0			250
19	0.85	130	2.3	800	4.9	370
20	1.04	100	2.4	700	4.9	500
21	1.25	130	1.8	800	4.9	600
22	1.40	160	2.8	1100	7.6	530
23	1.68	160	2.4	1100	7.6	620
			PBG–N=N–PBG			
24	0.64	80	1.9			350
25	0.85	120	5.1			450
26	0.85	120	2.7	800	5.3	450
27	2.90	240	3.4	1400	8.2	800
			PBG–$(CH_2)_{10}$–PBG			
28	1.40	190	2.4	1200	7.6	500
29	2.40	270	2.6	1600	9.5	600
30	2.50	280	2.0	1600	9.1	660
31	3.40	320	2.2	1700	9.0	680
32	4.20	400	1.2	2000	10.0	740
33	5.10	440	1.9	2100	10.0	750

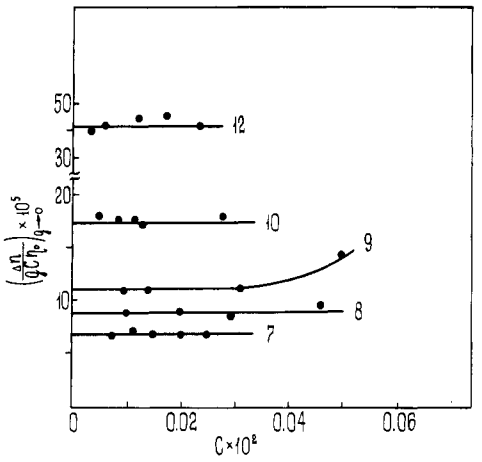


Figure 3. Concentration dependence of intrinsic FB $[\eta]$ for PBG samples in DMF. Figures at the curves are sample and fraction numbers in Table I.

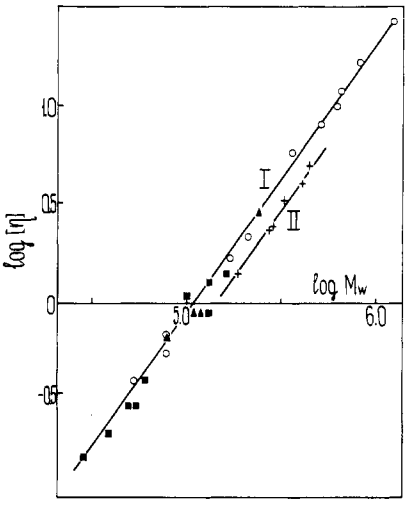


Figure 4. Logarithmic dependence of intrinsic viscosity $[\eta]$ on molecular weight M_w in DMF. The points represent experimental data for the samples: (○) PBG; (■) PBG–S–S–PBG; (▲) PBG–N=N–PBG; (+) PBG–$(CH_2)_{10}$–PBG. Curve 1 passes through points (○), and curve II passes through points (+).

the mean-square end-to-end distances $\langle h^2\rangle^{1/2}$ and $\langle h^2\rangle/M_w$.

For PBG the dependence of $[\eta]$ on M_w (Figure 4, curve I) processed by the least-squares method is described by the Mark–Kuhn–Houwink equation: $[\eta] = 6.72 \times 10^{-8} M^{1.42}$ in the 20-fold molecular weight range from 55×10^3 to 1100×10^3.

It was desirable to compare our results with those available in the literature for PBG. Figure 5 shows in the log $[\eta]$–log M system of coordinates the data obtained by several authors for PBG in spiralizing solvents[18-23] and the data obtained in the present paper. The straight line in Figure 5 is described by the above-mentioned Mark–Kuhn–Houwink equation. The value of the exponent $\alpha = 1.42$ obtained by us is in good agreement with the corresponding values obtained by Tsvetkov et al.[19] (1.40) and Norisuye et al.[20] (1.45), slightly differs from that obtained by Spach et al.[21] and Fujita et al.[22] ($\alpha = 1.54$), and markedly differs from that obtained by Doty et al.[23] ($\alpha = 1.70$).

For PBG samples containing groups –S–S– and –N=N–, the values of $[\eta]$ at equal M_w coincide to within the experimental value (10%) with the corresponding values for pure PBG. For PBG–$(CH_2)_{10}$–PBG, the dependence of $[\eta]$ on M_w (Figure 4, curve II) is described by the equation $[\eta] = 4.87 \times 10^{-8} M^{1.42}$ in the range $M_w = (190\text{–}440) \times 10^3$. The difference of the parameter K_η for PBG–$(CH_2)_{10}$–PBG from that for pure PBG can indicate a certain decrease in the equilibrium chain rigidity.

Strictly speaking, the investigated samples do not constitute a homologous series since according to the conditions of synthesis, each macromolecule regardless of its molecular weight contains only one joint. However, it was shown experimentally that in the molecular weight range investigated they behave as a homologous series. This made it possible to use with a certain restriction the persistent chain model for the description of conformational properties. However, we consider the value of persistence length a calculated from the experiment to be only "effective" because the physical model has no continuous curvature.

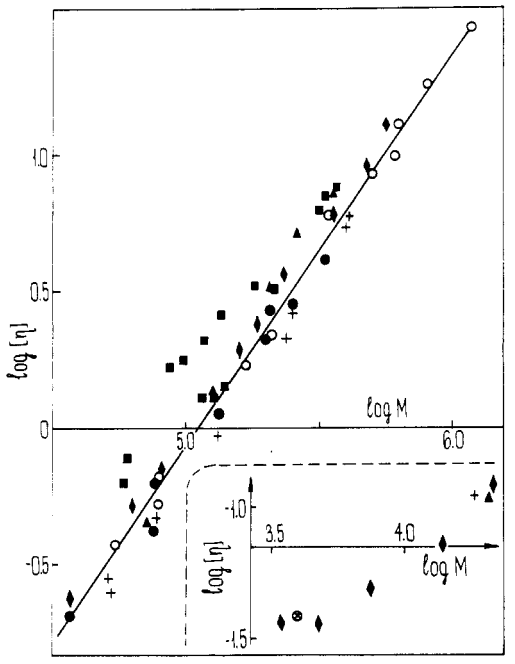


Figure 5. Logarithmic dependence of intrinsic viscosity $[\eta]$ on molecular weight M for PBG in spiralizing solvents. Published data: (■) ref 19; (♦) ref 20; (●) ref 21; (+) ref 22; (▲) ref 23. Data obtained in the present paper: (○) PBG; (⊗) PBG–S–S–PBG.

The values of A_2 for PBG agree with the published data.[18] These values make it possible to conclude that no appreciable thermodynamic differences exist in the PBG–DMF, (PBG–S–S–PBG)–DMF, (PBG–N=N–PBG)–DMF, and [PBG–$(CH_2)_{10}$–PBG]–DMF systems. Although for all the investigated samples $A_2 > 0$, the mean-square end-to-end distances of the chain $\langle h^2 \rangle^{1/2}$ obtained from the measurements of scattering asymmetry characterize the equilibrium rigidity of macromolecules because the swelling parameter for rigid-chain polymers is virtually equal to unity.[17] Tables I and II show that for all the investigated samples, the value of $\langle h^2 \rangle / M$ initially increases with M_w and then tends to saturation. This course of $\langle h^2 \rangle / M = f(M)$ corresponds to the theoretical dependence for a persistent chain model and indicates the high equilibrium rigidity of these samples.[25] In order to describe the hydrodynamic behavior of macromolecules, the theories of hydrodynamic properties of wormlike chains were applied. In these theories the drainage of polymer molecules is taken into account.[17,26,27] By extrapolation of $(M^2/[\eta])^{1/3}$ from $M^{1/2}$ proposed in ref 26 and with the assumption that the length of the projection of the monomer unit on the main-chain direction $\lambda = 1.5 \times 10^{-8}$ cm,[28] the value of the presistence length $a_{\eta,PBG} = 900 \pm 100$ Å and that of the effective persistence length $a_{\eta,PBG-(CH_2)_{10}-PBG} = 700 \pm 100$ Å were obtained Figure 6.

The diameter of the PBG chain $d = 30 \pm 3$ Å was determined from the intercept of the straight line with the ordinate by using for calculations the value of the hydrodynamic invariant $A_0 = 3.95 \times 10^{-10}$ g cm^2 s^2/(deg mol)$^{1/3}$.[17] The validity of this extrapolation has been shown for a broad class of rigid-chain polymers in the range of $L/A \geq 1$, where L is the length of a completely extended chain and A is the Kuhn segment.[26] For the samples investigated here, the L/A ratio ranges from 0.1 to 3.5. It is easy to show the correctness of this extrapolation in the range of $L/A < 1$ if the tabulated dependence of the Flory coefficient Φ on L/A in the ranges of $L/A < 1$ and $d/A = 0.01$ (where d is the chain diameter) is used.

Flow Birefringence. Table I shows that when M_w increases from 55×10^3 to 1100×10^3, the value of $\Delta n/\Delta\tau$ for PBG solutions increases by a factor of 5. In this case the value of $\Delta n/\Delta\tau$ at first increases with increasing M_w and subsequently tends to saturation. The dependence of $\Delta n/\Delta\tau$ on M_w at relatively high M_w indicates that PBG exhibits high equilibrium rigidity.[17,29] In order to obtain quantitative data on the rigidity of PBG molecules, the theory of the model for a kinetically rigid wormlike chain was applied.[17,29] The experimental data for PBG on $\Delta n/\Delta\tau = f(M)$ (Figure 7) were compared with the theoretical dependence $(\Delta n/\Delta\tau)/\beta BA = \varphi(x)$, where $\varphi(x) = x/(x+2)$, β is the anisotropy of unit length of the molecule, $B = (4\pi/45kT)/[(n^2+2)^2/n]$, and $x = L/a$. It is clear that the experimental points for PBG over the entire range of M_w fall on the theoretical curve $\varphi(x)$ at the value of persistence length $a = 1000$ Å and $\beta = 1 \times 10^{-16}$ cm^2 (curve 1). This value of a_{FB} indicates high equilibrium rigidity of PBG molecules. Similar results have been obtained in ref 24 for PBG solutions in dichloroethane in the range of $6 \times 10^4 < M_{SD}$. A certain difference between the $\Delta n/\Delta\tau$ values in the range of $M_w < 2 \times 10^5$ is observed.

Figure 7 also shows the experimental values of $\Delta n/\Delta\tau$ for the PBG–S–S–PBG and PBG–N=N–PBG samples vs M_w. These samples fill a relatively narrow M_w range, which makes it impossible to analyze completely the entire dependence of $\Delta n/\Delta\tau$ on M_w. However, taking into account experimental scattering, the points for PBG–S–S–PBG and PBG–N=N–PBG fall close to the theoretical curve for PBG. Hence, the application of the FB method, which is very sensitive to the degree of intramolecular order, did not reveal any important differences in the optical anisotropy of these samples.

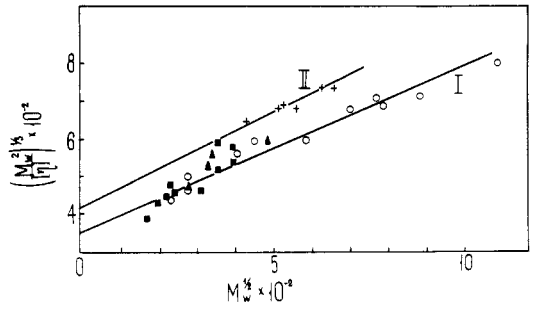


Figure 6. Dependence of $(M_w^2/[\eta])^{1/3}$ on $M_w^{1/2}$ in DMF. The points represent the experimental data for the samples: (○) PBG; (■) PBG–S–S–PBG; (▲) PBG–N=N–PBG; (+) PBG–$(CH_2)_{10}$–PBG. Curve I passes through points (○), and curve II passes through points (+).

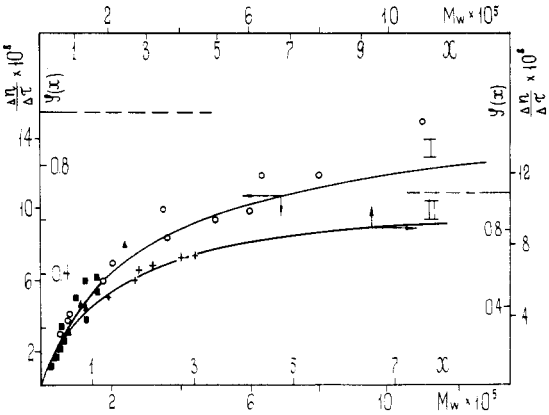


Figure 7. Dependence of shear optical coefficient $\Delta n/\Delta\tau$ on molecular weight M_w. The points represent the experimental data for the samples: (○) PBG; (■) PBG–S–S–PBG; (▲) PBG–N=N–PBG; (+) PBG–$(CH_2)_{10}$–PBG. The theoretical curves are plotted according to the equation[17,29] $\varphi(x) = (\Delta n/\Delta\tau)/\beta BA = x/(x+2)$ at $A = 2000$ Å (curve I) and at $A = 1400$ Å (curve II) at the same value of $\beta = 1 \times 10^{-16}$ cm^2.

For PBG–$(CH_2)_{10}$–PBG samples, the values of $\Delta n/\Delta\tau$ are lower than for PBG. Moreover, the shear optical coefficient in the investigated M_w range weakly depends on M_w and tends to saturation (Figue 7, curve II). It may be assumed that the optical anisotropies β of PBG and PBG–$(CH_2)_{10}$–PBG molecules coincide because the weight fraction of $(CH_2)_{10}$ groups in each PBG–$(CH_2)_{10}$–PBG molecule does not exceed 0.5%. In this case the experimental points for PBG–$(CH_2)_{10}$–PBG coincide with the theoretical curve $\varphi(x)$ at $\beta = 1 \times 10^{-16}$ cm^2 and $a_{FB} = 700$ Å.

The analysis of experimental data obtained in this work for PBG in DMF over a wide M_w range (55–1100) $\times 10^3$ shows that the values of persistence length a determined independently from viscometry and FB are close to each other ($a_\eta = 900 \pm 100$ Å, $a_{FB} = 1000 \pm 100$ Å) and are in good agreement with the published data.[17-19,21,24]

The theoretical calculation carried out by Wilemski[4] has shown that the decrease in equilibrium rigidity for the model of a once-broken rod may account to 15–37%, depending on the break angle θ.

The equilibrium rigidity of PBG–S–S–PBG and PBG–N=N–PBG determined in the present work coincided with that of PBG to within the experimental error. However, taking into account the fact that the experimental error is not lower than 10%, it is difficult to determine accurately the difference in a value that only changes by 10–15%.

In the case of PBG–$(CH_2)_{10}$–PBG, the equilibrium rigidity of molecules over the investigated M_w range is lower by 25–30% than that of PBG molecules (Figures 4, 6, and 7).

Hence, the comparative investigation of the molecular weight, the radius of gyration, the intrinsic viscosity, and the optical anisotropy of PBG molecules and its modified structures showed that the equilibrium rigidity of the modified PBG structures is determined by the chemical nature of the joint affecting the rotational mobility of its elements.

It is of interest to develop this investigation, introducing long and flexible joints with different degrees of polymerization into the PBG chain.

References and Notes

(1) Yu, H.; Stockmayer, W. H. *J. Chem. Phys.* **1967**, *47*, 1369.
(2) Hassager, O. *J. Chem. Phys.* **1974**, *60*, 2111.
(3) Taki, N.; Fujita, H. *Polym. J.* **1975**, *7*, 637.
(4) Wilemski, G. *Macromolecules* **1977**, *10*, 28.
(5) Teramoto, A.; Yamashita, T.; Fujita, H. *J. Chem. Phys.* **1967**, *46*, 1919.
(6) Nakagawa, K.; Nishioka, N.; Teramoto, A.; Fujita, H. *Polym. J.* **1973**, *4*, 332.
(7) Matsumoto, T.; Nishioka, N.; Teramoto, A.; Fujita, H. *Macromolecules* **1974**, *7*, 824.
(8) Vlasov, G. P.; Rudkovskaya, G. D.; Ovsyannikova, L. A.; Baranovskaya, I. A.; Sokolova, T. A.; Ulyanova, N. N.; Shestova, N. V. *Vysokomol. Soedin., Part B* **1980**, *22*, 216.
(9) Vlasov, G. P.; Rudkovskaya, G. D.; Ovsyannikova, L. A. *Makromol. Chem.* **1982**, *183*, 2635.
(10) Blout, B. R.; Karlson, R. H. *J. Am. Chem. Soc.* **1956**, *78*, 941.
(11) Fuller, W. D.; Verlander, M. S.; Goodman, M. *Biopolymers* **1976**, *15*, 1869.
(12) Vlasov, G. P.; Ovsyannikova, L. A.; Rudkovskaya, G. D.; Komogorova, T. A.; Sokolova, T. A.; Shepelevsky, A. A. Authors' Certificate 664970 USSR (*Biull. Izobret.* **1979**, *20*, 91).
(13) Gritsenko, F. R.; Spirin, Yu. L.; Grishenko, V. K.; Kochetkova, T. I. *Dokl. Akad. Nauk SSSR* **1974**, *214*, 569.
(14) Sekiguchi, H. *Pure Appl. Chem.* **1981**, *53*, 1689.
(15) Frisman, E. V.; Shchagina, L. V.; Vorobiev, V. I. *Kolloid Zh.* **1965**, *27*, 130.
(16) Eskin, V. E. *Rassejanie sveta rastvorami polimerov i svoistva makromolekul*; Nauka: Leningrad, 1986.
(17) Tsvetkov, V. N. *Zhestkotsepnye polimernye molekuly*; Nauka: Leningrad, 1986.
(18) Teramoto, A.; Fujita, H. *Adv. Polym. Sci.* **1975**, *18*, 65.
(19) Tsvetkov, V. N.; Mitin, Yu. V.; Shtennikova, I. N.; Glushenkova, V. R.; Skazka, V. S.; Nikitin, N. A. *Vysokomol. Soedin., Part A* **1965**, *7*, 1098.
(20) Itou, S.; Nishioka, N.; Norisuye, T.; Teramoto, A. *Macromolecules* **1981**, *14*, 904.
(21) Spach, G.; Freund, L.; Daune, M.; Benoit, H. *J. Mol. Biol.* **1963**, *7*, 468.
(22) Fujita, H.; Teramoto, A.; Okita, K.; et al. *Biopolymers* **1966**, *4*, 769.
(23) Doty, P.; Bradbery, J.; Holtser, A. *J. Am. Chem. Soc.* **1956**, *78*, 947.
(24) Tsvetkov, V. N.; Shtennikova, I. N.; Ryumsev, E. I.; Okhrimenko, G. I. *Vysokomol. Soedin., Part A* **1965**, *7*, 1104.
(25) Porod, G. *Monatsh. Chem.* **1949**, *2*, 251.
(26) Bushin, S. V.; Tsvetkov, V. N.; Lysenko, E. B.; Emelyanov, V. N. *Vysokomol. Soedin., Part A* **1981**, *23*, 2494.
(27) Yamakawa, H.; Fujii, M. *Macromolecules* **1974**, *7*, 128.
(28) Yamaoka, K.; Yamamoto, Sh.; Kosako, I. *Polym. J.* **1987**, *19*, 951.
(29) Tsvetkov, V. N. *Dokl. Akad. Nauk SSSR* **1982**, *266*, 670.