Rheological Properties of Rodlike Polymers in Solution

III. Transient and Steady-State Studies on Nematic Solutions

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ABSTRACT: Rheological studies are reported on nematic solutions of the rodlike macroion poly(14-phenylene-2,6-benzobisthiazole), PBT. The data reported include the steady-state viscosity η_κ and recoverable compliance R_κ as functions of the shear rate κ , the creep compliance $J_\sigma(t)$ and the recoverable compliance $R_\sigma(t)$ determined with shear stress σ , and the viscosity growth function $\eta_\kappa(t)$ determined with shear rate κ . The nematic solutions did not exhibit true linear viscoelastic behavior in the range studied ($\sigma \geq 14$ Pa and $\kappa \geq 10^{-4}$ s⁻¹). Neither was any “yield behavior” observed over this range. The steady-state parameters are discussed in terms of a single-integral constitutive equation of the BKZ-type in which the relaxation times are estimated from data on $R_\sigma(t)$ at small σ .

KEY WORDS Flow Birefringence / Nematic Solution / Rodlike Polymer / Rheology / Nonlinear Creep /

In Parts 1 and 2 of this series,^{1,2} the rheological and rheo-optical properties of mesogenic solutions of rodlike macrions are reported for conditions of concentration, rod length and temperature for which the solutions are optically isotropic. Steady-state and transient properties are reported in parts I and II, respectively, and discussed in terms of a single-integral constitutive equation and molecular theories. Here, some steady-state and transient rheological properties will be presented for nematic solutions of two samples of one of the polymers studied in Parts I and II, namely, poly(1,4-phenylene-2,6-benzobisthiazole), PBT. The data to be reported include the steady-state viscosity η_κ and recoverable compliance R_κ as functions of the shear rate κ , the creep compliance $J_\sigma(t)$ and recoverable compliance $R_\sigma(t)$ determined with shear stress σ , and the viscosity growth function $\eta_\kappa(t)$ determined with shear rate κ .

The transient function (*i.e.*, $J_\sigma(t)$, $R_\sigma(t)$ and $\eta_\kappa(t)$) are defined in Part II. In Part II, the limiting values $R_0(t)$ of $R_\kappa(t)$ at small σ , and $\eta_0(t)$ of $\eta_\kappa(t)$ at small κ were expressed in terms of retardation and relaxation times, respectively, as³:

$$R_0(t) = R_0 - \sum_1^{n-1} R_i \exp(-t/\lambda_i) \quad (1)$$

$$\eta_0(t) = \eta_0 - \sum_1^n \eta_i \exp(-t/\tau_i) \quad (2)$$

where, of course, the set of η_i and τ_i may be determined from the set of R_i and λ_i together with R_0 and $\tau_c = R_0\eta_0$, and *vice versa*. In Part II it was found that a single-integral relation for the shear stress $\sigma(t)$ given by^{2,4}

$$\sigma(t) = \sum \eta_i \tau_i^{-2} \int_0^\infty \Delta\gamma(t, u) F[\Delta\gamma(t, u)] \exp(-u/\tau_i) du \quad (3)$$

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could be used to predict η_κ and R_κ . Here $\Delta\gamma(t, u) = \gamma(t) - \gamma(t-u)$ and $F(\gamma)$ is given by the expression

$$F(\gamma) = \exp[-m(|\gamma| - \gamma')/\gamma''] \quad (4)$$

where m is zero for $|\gamma| < \gamma'$ and unity otherwise, with γ' and γ'' material parameters. Of course, if $F(\gamma)$ is unity (*i.e.*, $|\gamma| < \gamma'$, then eq 3 reduces to the result for the linear Boltzmann constitutive equation. With eq 3 and 4,⁴

$$\eta_\kappa = \sum \eta_i (1 - q_{\kappa,i}) \quad (5)$$

$$\eta_0 R_\kappa \approx \sum \eta_i \tau_i [1 - q_{\kappa,i} \exp(-\eta_\kappa R_\kappa / \tau_i)] \quad (6)$$

where

$$q_{\kappa,i} = (1 + \alpha f_i^2 - f_i) \exp(-g_i) \quad (7)$$

with $f_i^{-1} = 1 + \alpha g_i^{-1}$, $g_i = \gamma' / \tau_i \kappa$ and $\alpha = \gamma' / \gamma''$. These relations provided satisfactory fits to data on η_κ and R_κ , given experimental data on η_i and τ_i for the isotropic solutions. Based on studies² of $J_\sigma(t)$, γ' was found to be inversely proportional to c . Mechanistic models with results similar to eq 3 and 4 are discussed in Part II.^{2,5,6} These differ from experiment principally in predicting a far narrower distribution of τ_i (or λ_i) than found in our studies.

For the data in Parts I and II, dependence of η_0 on c and the rodlength L was given by the expression^{1,2,5}

$$\eta_0 / \eta_s = K N_A^2 [\eta] \alpha^* X^3 (1 - BX)^{-2} \quad (8)$$

for $X < 1$, where $X = cL / M_L \alpha^*$, with $M_L = M / L$, $[\eta]$ is the intrinsic viscosity and α^* / B and K are parameters of the models. Of the latter, B is expected to be nearly unity,⁵ $\alpha^* M_L / L$ is expected to be nearly equal to the concentration c_c required to form a nematic phase, and the original calculation⁵ gave $K \sim 1$. With the data reported in Parts I and II, the former two predictions are verified, but

$K \approx 1.5 \times 10^{-4}$, in better agreement with revised estimates.⁷

EXPERIMENTAL

The materials and methods used are described fully in Parts I and II. The polymers used in this study are listed in Table I. Sample PBT-53 was studied in solution in methane sulfonic acid (MSA), and PBT-62 was studied in solution in MSA containing 3 weight percent chlorosulfonic acid. The range of the weight fraction w and temperature T spanned in the studies is given in Table I, and shown schematically in Figures 1 and 2. With PBT-62, only steady-state data were obtained, *e.g.*, η_κ and R_κ . With PBT-53, in addition to the steady-state data, experiments included $J_\sigma(t)$, $R_\sigma(t)$ and $\eta_\kappa(t)$.

RESULTS

The systematic effects observed on η_κ and R_κ are illustrated in Figures 3 and 4, respectively, for several concentrations of PBT-62 for $T \approx 60^\circ\text{C}$ and for a solution of PBT-53 for $T \approx 23^\circ\text{C}$. The limiting values η_0 and R_0 obtained for η_κ and R_κ , respectively, at small κ are listed in Table II.

As may be seen in Figures 3 and 4, in some cases η_κ did not go to a limiting value at small κ with the nematic solutions—this feature is discussed further in the next section. In such cases, R_κ did tend to a constant value R_0 at small κ , and usually a range of κ existed for which η_κ was essentially a constant, designated η_p . Values of R_0 and η_p are entered in Table II for the nematic fluids.

The data on η_0 are reduced to 24°C using $\partial \ln \eta / \partial T^{-1}$ given in Part II. For the isotropic solution, $\partial \ln \eta / \partial T^{-1}$ is about equal to $\partial \ln \eta_s w_c^3 / \partial T^{-1}$, as expected with eq 8, where w_c is the concentration required to form a stable nematic phase. For the nematic solution, $\partial \ln \eta / \partial T^{-1}$ is smaller, and more nearly equal to $\partial \ln \eta_s / \partial T^{-1}$. Consequently, data on η_p are reduced to 24°C using $\partial \ln \eta_s / \partial T^{-1}$.

Additional data on η_κ and R_κ for PBT-62 and data for PBT-53 are given in Figures 5–11, in plots of the reduced functions $\eta_\kappa / \eta_0 (\eta_\kappa / \eta_p)$ and R_κ / R_0 versus $\eta_0 R_0 \kappa$ (or $\eta_p R_0 \kappa$). Except for data on nematic solutions with $\eta_p R_0 \kappa < 1$, these plots are independent of T for a given concentration.

Data on $J_\sigma(t)$ versus t are given in Figure 12 for a nematic solution of PBT-53 ($w = 0.0323$ at 19°C).

Table I. Polymers used in this study

Polymer	$[\eta]$	L_η^a	Range w	Range T
	ml g ⁻¹	nm	g kg ⁻¹	K
PBT-62	2,650	170	15.0–82	272–353
PBT-53	1,400	120	25.5–42.7	283–333

^a $L_\eta = M_\eta / M_\eta$, where $M_L = 220$ dalton nm⁻¹ and $M_\eta = ([\eta] / K_\eta)^{1.8}$ with $M_L^{1.8} K_\eta = 0.26$ ml g⁻¹.

The behavior is similar to that reported for an isotropic solution of PBT-53 ($w=0.0255$ at 30°C) discussed in Part II. As with the latter, $J_\sigma(t)$ is found to equal the limiting behavior $J_0(t)$ for small σ provided the strain $\gamma(t)=\sigma J_\sigma(t)$ is less than a critical value γ^* , as indicated on Figure 12. The recoverable compliance function $R_\sigma(t)$ obtained following steady-state deformation is also shown in Figure 12 for one shear stress ($\sigma=14.6$ lowering steady-state

deformation is also shown in Figure 12 for one shear stress ($\sigma=14.6$ Pa).

Data on $\sigma(t)$ as a function of the strain κt in a stress growth experiment are given in Figures 13 and 14. In these experiments κ is constant for κt

Figure 1. Schematic diagram showing the concentration (weight fraction w) and temperature used in rheological studies on solutions of PBT-53. Regions of isotropic and nematic solutions are indicated in the diagram.

Figure 2. Schematic diagram showing the concentrations (weight function w) and temperatures used in rheological studies on solutions of PBT-62. Conditions of w and T for which solutions were observed to be isotropic or nematic are indicated by I or N, respectively. Data for conditions to the left and right sides of the dashed line are given in Figures 5 and 9, respectively.

Figure 3. The steady-state viscosity of η_κ for solutions of PBT-53 with $T \approx 20^\circ\text{C}$. The symbols indicate $w/\text{g kg}^{-1}$ of 25.5, $\circ$; 29.4, $\circ$; 32.3, $\circ$ and 42.7, $\circ$.

Figure 4. The steady-state viscosity η_κ and recoverable compliance R_κ for solutions of PBT-62 with $T \approx 60^\circ\text{C}$. The symbols indicate w as in Figure 2.

greater than about 0.3, but owing to instrumental limitations, $\gamma(t) \leq \kappa t$ for smaller κt . The data reveal a maximum in $\sigma(t)$ with increasing t such that $\partial\sigma(t)/\partial t$ is zero for κt equal to a value γ^+ that is nearly independent of κ , and smaller than γ^* determined from $J_\sigma(t)$. Values of γ^* and γ^+ determined for isotropic and nematic solutions over a range of c are given in Figure 15.

DISCUSSION

The decrease of "the viscosity" on the formation of the nematic phase is one of the most characteristic features noted for mesogenic polymer solutions.⁸ The value of η_κ usually referred to in this correlation is η_P defined above. Values of η_P determined here are given in Figure 16, along with values of η_0 for isotropic solutions reported in Parts I and II; as mentioned above, the latter are well represented by eq 8. In a theoretical treatment related to that used to derive eq 8, Doi has calculated the steady-state viscosity η_{aniso} for a "uniform" fluid, in a "weak velocity gradient."⁹ The fluid is characterized by an order parameter S related to the ratio c/c_c :

$$S = \frac{1}{4} + \frac{3}{4} \left(1 - \frac{8}{9} \frac{c_c}{c} \right)^{1/2} \quad (9)$$

Table II. Rheological parameters for solutions of rodlike polymers

Polymer	w g kg^{-1}	T K	$\eta_0 A^{-1}$ kPas ^a	$R_0 c R T / M_\eta$ ^b
53	25.5 (I) ^c	333	1.89	(60)
	25.5 (I)	313	1.83	(60)
	25.5 (I)	303	1.73	(62)
	25.5 (I)	296	2.10	64
	25.5 (I)	286	1.89	69
	29.4 (I)	313	7.15	70
	29.4 (I)	296	7.64	78
	29.4 (I)	285	6.80	107
	32.3 (I)	333	4.83	102
	32.3 (N)	316	4.05	97
	32.3 (N)	294	4.34	112
	32.3 (N)	283	6.90	130
	42.7 (N)	316	12.3	190
	42.7 (N)	296	11.0	180
	42.7 (N)	284	9.6	172
62	15.0 (I)	333	0.28	18
	15.0 (I)	318	0.31	17
	15.0 (I)	293	-0.27	21
	25.2 (I)	333	22.8	42
	25.2 (I)	297	41.0	31
	25.2 (I)	277	52.0	18
	30.0 (I)	353	45.6	63
	30.0 (I)	333	41.7	53
	30.0 (I)	313	60.4	44
	30.0 (I)	293	74.7	35
	30.0 (I)	283	86.4	30
	30.0 (I)	272	71.1	23
	34.3 (I)	333	13.2	31
	34.3 (I)	313	13.1	21
	34.3 (N)	293	3.1	33
	34.3 (N)	283	3.0	25
	47.3 (N)	333	0.61	940
	47.3 (N)	313	0.53	970
	61.1 (N)	333	0.94	2030
	82.0 (N)	333	0.83	3630
	82.0 (N)	297	0.47	3640

^a $A = \exp E(T^{-1} - T_r^{-1})$ with $T_r = 297\text{ K}$ and E/K equal to 4065 for isotropic solutions, and 2800 for nematic solutions, see the text.

^b R_0 in parenthesis calculated as τ_c/η_0 with τ determined from fit of η_κ/η_0 versus $\tau_c\kappa$.

^c Symbols I and N indicate solutions which were isotropic or nematic at rest, respectively.

for $c/c_c > 8/9$ and zero for smaller c . With this model, for $c > c_c$,

$$\eta_{\text{aniso}} = \eta_{\text{iso}}(c_c) D(S) \quad (10)$$

Figure 5. η_κ/η_0 and R_κ/R_0 versus $R_0\eta_0\kappa$ for isotropic solutions of PBT-53 ($w = 25.5$ g/kg, with symbols as in Figure 1). The curves for η_κ/η_0 and R_κ/R_0 represent eq 5 and 6, respectively, with the τ_i and η_i in Table III.

Figure 6. η_κ/η_0 and R_κ/R_0 versus $R_0\eta_0\kappa$ for isotropic solutions of PBT-62 (symbols as in Figure 2). The dashed curve represents R_κ/R_0 vs. $\tau_c\kappa$ from Figure 5.

where $\eta_{\text{iso}}(c_c)$ is the viscosity of an isotropic solution at concentration c_c , given by eq 8 and $D(S)$ decreases with increasing S :

$$D(S) = (1-S) \left(\frac{1+S}{1+2S} \right)^2 \frac{1+3S/2}{(1+S/2)^2} \approx (1-S)/(1+S/2)^2 \quad (11)$$

With eq 10, $\eta_{\text{aniso}}/\eta_{\text{iso}}(c_c)$ is expected to depend on c/c_c through the dependence of S on c/c_c . The data in Figure 16 conform qualitatively to eq 10 in that

η_p decreases from $\eta_{\text{iso}}(c_c)$ with increasing c/c_c , but η_p appears to level and then increase with larger c/c_c , whereas $D(S)$ decreases monotonically with increasing c/c_c .

The continuous increase of η_κ with decreasing κ in experiments observed with most of the nematic solutions is similar to behavior reported previously in our laboratory¹⁰ for nematic solutions of poly(1,4-phenylene-2,6-benzobisoxazole) and poly(1,4-phenylene terephthalate), as well as by a num-

Figure 7. η_κ/η_0 (or η_κ/η_0) and R_κ/R_0 versus $R_0\eta_0\kappa$ (or $R_0\eta_p\kappa$) for isotropic (or nematic) solutions of PBT-53 ($w=32.3$ g kg⁻¹, with symbols as in Figure 1). The solid curves for η_κ/η_0 and R_κ/R_0 represent eq 5 and 6, respectively with the τ_i and η_i given in Table III. The dashed curve shows $R_0(t)/R_0$ versus τ_c/t .

Figure 8. η_κ/η_p and R_κ/R_0 versus $R_0\eta_0\kappa$ for nematic solutions of PBT-53 ($w=42.7$ g kg⁻¹, with symbols as in Figure 1). The dashed curves represent the curves given in Figure 7.

ber of others (see the discussion in ref 8). The behavior is not always observed over the range of κ studied,⁸ and indeed, is not observed here with the nematic solution of PBT-53 with $w=42.7$ g kg⁻¹. The transient behavior discussed in the following

for $J_\sigma(t)$ at small σ and $\eta_\kappa(t)$ at small κ displays unusual behavior in the range for which η_κ increases with increasing κ .

As shown in Figures 13 and 14, in a stress-growth experiment for the nematic solutions studied, for

Figure 9. η_κ/η_p and R_κ/R_0 versus $R_0\eta_p\kappa$ for nematic solutions of PBT-62 (symbols as in Figure 2). The curves represent the behavior shown in Figure 6.

Figure 10. η_κ/η_p and R_κ/R_0 versus $R_0\eta_p\kappa$ for solutions of PBT-62 (symbols as in Figure 2). The curves represent the behavior shown in Figure 6.

small κ the stress $\sigma(t)$ increases monotonically with increasing strain κt . In the creep behavior obtained with a nematic solution (Figure 12), the strain $\gamma(t) =$

$\sigma J_\sigma(t)$ increases monotonically with increasing t , so that at large t , $\gamma(t) \approx \sigma t / \eta_\kappa$ and $\partial \gamma(t) / \partial t$ is a constant. In neither case is there any indication of solid-like

Figure 11. η_{κ}/η_0 and R_{κ}/R_0 versus $R_0\eta_0\kappa$ for solutions of PBT-62 (symbols as in Figure 2). The dashed curves represent the behavior shown in Figure 6.

Figure 12. Creep $J_{\sigma}(t)$ and recoverable compliance $R_{\sigma}(t)$ versus t/τ_c (with $\tau_c = 170$ s) for a nematic solution of PBT-53 ($w = 32.3$ g kg⁻¹, $T = 19.5^{\circ}\text{C}$). Values of shear stress σ /Pa used are given, along with the parameter γ^* .

behavior at small strain—i.e., no yield phenomenon is observed. For values of σ such that $\partial\gamma(t)/\partial t$ at steady-state is in the range of κ for which stress-

growth experiments give $\eta_{\kappa} \approx \eta_p$, the creep and stress-growth experiments give the same steady-state viscosity η_p , as would normally be expected.

Figure 13. The stress $\sigma(t)$ in a stress-growth experiment *versus* the strain κt for a solution of PBT-53 ($w = 32.3 \text{ g kg}^{-1}$) at temperatures for which the solution is isotropic (43°C) and nematic (19.5°C). Values of $\kappa/\dot{\gamma}$ are indicated.

Figure 14. The stress $\sigma(t)$ in a stress-growth experiment *versus* the strain κt for a nematic solution of PBT-53 ($w = 42.7 \text{ g kg}^{-1}$) at two temperatures.

Figure 15. The critical strains γ^* and γ^+ plotted (as the inverse) *versus* the concentration w for solutions of PBT-53.

However, different behavior is obtained, for very small κ , for which stress-growth experiments give a larger steady-state viscosity, *i.e.*, $\eta_\kappa > \eta_p$. For example, with PBT-53 at $w = 34.3 \text{ g kg}^{-1}$, $\eta_\kappa \approx 2.4 \eta_p$ for $\kappa = 3.8 \times 10^{-4} \text{ s}^{-1}$ (*i.e.*, $\eta_p R_0 \kappa = 0.053$). For this sample, a creep experiment effected at σ such that $\partial\gamma(t)/\partial t = 3.8 \times 10^{-4} \text{ s}^{-1}$ at steady-state resulted in a smaller steady-state viscosity, $\eta_\kappa = 1.2\eta_p$. Values of R_0 determined after steady-state flow in these experiments were equivalent. In a creep experiment, $\partial\gamma(t)/\partial t$ is larger at small t than at steady-state (*i.e.*, large t). Thus, in the example cited the reduced η_κ obtained in creep is in the range expected for a stress-growth experiment with κ equal to $\partial\gamma(t)/\partial t$ obtained at small t in the creep experiment. The quiescent, relaxed nematic fluids studied here are characterized by a texture such that locally, the axes of the rodlike chains are parallel, but with no

Figure 16. Left side: $\eta_0/M_w[\eta](a^*/a_0^*)^3$ versus $BcL_w/M_L a^*$ for isotropic solutions of PBT-53, PBT-62 and other rodlike polymers (see Part II for identification of the symbols). Here B/a^* is obtained by comparison of eq 8 with experiment (see Part II), and B/a_0^* is an arbitrary constant. Right side: The same quantities for nematic solutions of PBT-62 (○) and PBT-53 (●—).

correlation among these axes over the entire sample. The behavior of η_κ at small κ or σ may be caused by effects on this texture. In particular, domains with the molecular axes of the rodlike chains oriented perpendicular to the flow plane may be depopulated with increasing κ (or $\partial\gamma(t)/\partial t$), resulting in reduced η_κ . A similar suggestion has been made on the basis of flow birefringence data.¹¹ If this view is correct, then comparison of η_p with η_{aniso} may be inappropriate, since the latter is computed for a uniform fluid whereas η_p could be for fluid with the molecular axes oriented preferentially in the flow plane, so that one could have $\eta_p < \eta_{\text{aniso}}$, as the Miesowicz viscosities are unequal.^{12,13} The failure to observe an increase in η_κ with decreasing κ for some nematic fluids (e.g., PBT-53 with $w = 42.7 \text{ g kg}^{-1}$) may indicate suppressed domain structure (perhaps owing to incomplete relaxation of prior deformation) or insufficiently small κ to observe the effect.

With increasing κ , the $\sigma(t)$ obtained in stress-growth experiments display a maximum for strain κt about equal to a constant γ^+ (independent of κ) for a given c — γ^+ appears to decrease slowly with increasing c . This behavior is not unusual, and is observed with isotropic solutions of the polymers

Table III. Retardation and relaxation spectra

λ_i/τ_c	R_i/R_0	τ_i/τ_c	η_i/η_0
PBT-53; $w = 32.3 \text{ g kg}^{-1}$ (Nematic) ^a			
8.30	0.262	8.59	0.037
2.65	0.104	2.79	0.065
1.04	0.312	1.40	0.266
0.193	0.170	0.353	0.323
		0.086	0.149
0.042	0.111	0.0075	0.160
PBT-53; $w = 29.4 \text{ g kg}^{-1}$ (Isotropic) ^b			
2.580	0.580	3.251	0.231
0.210	0.280	0.494	0.480
0.0175	0.130	0.0615	0.092
		0.0010	0.092
PBT-53; $w = 25.5 \text{ g kg}^{-1}$ (Isotropic)			
5.248	0.430	5.732	0.094
1.022	0.290	1.354	0.258
0.240	0.174	0.381	0.253
0.080 ₅	0.035	0.098 ₈	0.084
		0.025 ₂	0.312

^a R_0 , η_0 , and τ_c replaced by values obtained from creep with shear stress $\sigma = 14.6 \text{ Pa}$, see the text; $\tau_c = \eta_0 R_0$.

^b See Part II.

studied here, with γ^+ being slightly larger for the latter. Similarly, with increasing σ , the $\gamma(t)$ obtained in creep experiments are given by $\sigma J_0(t)$ provided $\gamma(t)$ is smaller than a constant γ^* (independent of σ) for a given c , with $\gamma(t) > \sigma J_0(t)$ for larger $\gamma(t)$. This is similar to behavior obtained with isotropic solutions of the rodlike chains,² with γ^* being somewhat smaller for the nematic solution than for the isotropic fluids. The combined behavior for stress-growth and creep suggests that as with eq 3, the rheological constitutive equation for nematic fluids may involve a critical strain criterion. The behavior at small κ (or σ) suggests that eq 3 may not itself suffice.

With the nematic fluids studied here, no proper linear viscoelastic behavior was observed, so that the τ_i (or λ_i) distribution could not be rigorously determined. Nevertheless, since for the nematic solutions, η_κ and R_κ are (nearly) independent of κ over a reasonable range of κ for $R_0\eta_p\kappa$, in the range 0.1 to 1, it is reasonable to compute (apparent) values of R_i and λ_i from data in $R_\kappa(t)$ for corresponding levels of σ . Values of R_i and λ_i determined for the data on $R_\kappa(t)$ in Figure 12 are given

Figure 17. $R_\sigma(t)/R_0$ versus t/τ_c for two isotropic solutions of PBT-53 ($w/\text{g kg}^{-1}$ equal to 25.5 and 29.4, long and short dash, respectively) and a nematic solution ($w = 32.3 \text{ g kg}^{-1}$, $T = 19.5^\circ\text{C}$, solid curve). For the latter, τ_c is replaced by $\eta_\kappa R_\kappa$ and R_0 is replaced by R_κ . With the isotropic solutions, $R_\sigma(t) = R_0(t)$, and with nematic solution, $\sigma = 14.6 \text{ Pa}$.

in Table III—the data are normalized by the values of R_κ and η_κ obtained with the σ used to determine $R_\sigma(t)$ (i.e., $\sigma = 14.6 \text{ Pa}$). Of course, the data in Table III reproduce $R_\sigma(t)$ in Figure 12. Their use to estimate η_κ and R_κ will be discussed below. The set of λ_i for the nematic solution is similar in breadth to those obtained with an isotropic solution on PBT-53 ($w = 29.4 \text{ g kg}^{-1}$), given in Table III for comparison, so that as shown in Figure 17, $R_0(t)/R_0$ for the latter is similar to $R_\sigma(t)/R_\kappa$ for the nematic solution. By comparison, $R_0(t)/R_0$ and the λ_i set for a solution of PBT-53 ($w = 25.5 \text{ g kg}^{-1}$) are noticeably different.

As shown in Part II, for isotropic solutions, η_κ/η_0 and R_κ/R_0 may be represented in terms of eq 5 and 6 given the parameters η_i and τ_i (or R_i and λ_i). With these fluids (as with flexible chain polymers⁴) over a wide range $\tau_c\kappa$ (with $\tau_c = \eta_0 R_0$), the approximations

$$\eta_\kappa \simeq [\eta_0(t)]_{\kappa t=1} \quad (12)$$

$$R_\kappa \simeq [R_0(t)]_{\kappa t=1} \quad (13)$$

provide direct correspondence between linear and nonlinear properties. In particular, with a narrow distribution of τ_i , R_κ is essentially independent of $\tau_c\kappa$ over a wide range of $\tau_c\kappa$. With the isotropic solutions studied here, the distribution of τ_i is reasonably broad, so that R_κ decreases markedly with increasing $\tau_c\kappa$, as discussed in Part II, in good agreement with eq 13. Similar behavior is shown in Figure 7 for a nematic solution, where $R_\sigma(t)$ for a low σ corresponding to the range for which $\eta_\kappa \approx \eta_P$

and $R_\kappa = R_0$. As mentioned above, for the isotropic solutions the functions η_κ/η_0 and R_κ/R_0 versus $\tau_c\kappa$ are independent of T for a given material. In the interests of completeness, reduced curves for isotropic solutions of PBT-53 and 62 given in Parts I and II are included in Figures 5 and 6. For PBT-53, η_κ/η_0 and R_κ/R_0 are fitted well by eq 5 and 6, respectively, using η_i and τ_i determined by linear viscoelastic studies. As may be seen in Figure 6, the decrease of R_κ/R_0 with increasing $\tau_c\kappa$ is more pronounced with the isotropic solutions of PBT-62 than those of PBT-53, indicating a broader τ_i (or λ_i) distribution with the PBT-62 solutions.

The set of τ_i and η_i given in Table III for the nematic solution with $w = 32.3 \text{ g kg}^{-1}$ were computed from the λ_i and R_i given in Table III. The τ_i and η_i were calculated using the expressions for linear viscoelasticity, despite the nonlinearity discussed in the preceding. The functions η_κ/η_P and R_κ/R_0 versus $R_0\eta_P\kappa$ computed using these τ_i and η_i in eq 5 and 6 are shown in Figure 7—these curves were computed with $\gamma' = 1.0$ and $\gamma'' = 2.4$, in accord with the experimental data. The computed R_κ/R_0 are in good accord with the experimental η_κ/η_P ; the computed R_κ/R_0 tend to lie 20–40% above the measured values for large $R_0\eta_P\kappa$. Apparently, the quasi-linear treatment of the data used to estimate τ_i and η_i , etc., is useful in the range studied here, provided $R_0\eta_P\kappa$ is at least as large as the value needed to obtain the “plateau” in η_κ (e.g., $R_0\eta_P\kappa > 0.1$ for PBT-53 with $w = 32.3 \text{ g kg}^{-1}$).

It may be noted that the treatment given above would not lead to negative first normal stress $v_{\kappa i}^{(1)}$ as has been reported for an ordered solution of poly(γ -benzyl glutamate), (PBG). Thus, with the single-integral equation used to obtain eq 5 and 6, the reduced parameter $N_\kappa^{(1)} = v_{\kappa i}^{(1)}/2(\kappa\eta_\kappa)^2$ is given by

$$\eta_\kappa^2 N_\kappa^{(1)} = \sum \eta_i \tau_i (1 - q_{\kappa, i} P_{\kappa i}) \quad (14)$$

where $P_{\kappa, i}$ is a function of g_i and α (see Part II). With eq 14, $N_\kappa^{(1)}$ is always positive. Data were obtained in our laboratory on a solution of PBLG in cresol for which negative values of $N_\kappa^{(1)}$ were obtained¹⁴—the solution was provided by R. S. Porter. The results for η_κ , given in Figure 18 were in good agreement with data reported by Porter and Kiss over the range of κ for which the data overlapped. Data obtained here at lower κ did not become independent of κ . Values of R_κ were found to decrease smoothly with increasing κ , through the

Figure 18. $\eta_\kappa(\tau_{20}/\tau_T)$, R_κ and $N_\kappa^{(1)}$ versus $(\tau_T/\tau_{20})\kappa$ for an anisotropic solution of poly(γ -benzyl glutamate) in cresol for T/K equal to 273 (Δ , $\blacktriangle$) and 293 ($\circ$, $\bullet$). The dashed line and the data on $N_\kappa^{(1)}$ are from reference 12. The factor τ_T/τ_{20} is unity for $T=293$ K and chosen to superpose data on R_κ versus $(\tau_T/\tau_{20})\kappa$ for $T=273$ K. The range denoted " $N_\kappa^{(1)}$ anomaly" designates the range for negative $N_\kappa^{(1)}$ according to ref 14.

range of κ for which $N_\kappa^{(1)}$ reported to be negative. On the basis of the behavior observed for η_κ and R_κ , one can speculate that the τ_i (or λ_i) distribution would be very broad for the PBG solution. With eq 5 and 14, $N_\kappa^{(1)}$ may become very small with η_κ/η_0 not too much less than unity with some τ_i -distribution, but $N_\kappa^{(1)}$ will always be positive.

With a PBT-62 solution studied for which c was slightly less than c_c so that the quiescent fluids were (macroscopically) isotropic, the data on η_κ versus κ did not display any range of κ for which η_κ was independent of κ . Rather, as shown in Figures 4 and 10, η_κ decreased slowly with increasing κ at small κ . For these solutions, the decrease in R_κ with increasing κ was much smaller than observed with isotropic solutions (see Figure 10). This behavior, which is found only over a narrow range of conditions with c close to, but less than c_c , may be caused by a tendency for the isotropic solutions to develop orientational order characteristic of the nematic state under the influence of a shear stress, so that η_κ decreases slowly with increasing κ .

As shown in Figure 11, the data on η_κ/η_0 versus $\tau_c\kappa$ for solution with c near c_c for the temperature of the measurement do not superpose with each other and differ from data on the isotropic solutions at lower c . For example, with PBT-62, the data on η_κ/η_0 versus $\tau_c\kappa$ for the solution with $w/g\text{ kg}^{-1}$ equal to 30.0 and 34.3 do not superpose over the temperature range studied. In terms of eq 5 or 6, it appears that the distribution of τ_i sharpens with decreasing T for this solution. The behavior of R_κ/R_0 , which becomes nearly independent of $\tau_0\kappa$ at low T , is also consistent with an effectively narrowed distribution of τ_i .

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