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Measurement of the Linear Viscoelastic Behavior of Antimisting Kerosene

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ABSTRACT

Measurements of dynamic viscoelastic properties in very small oscillating shear deformations have been made on solutions of a jet fuel, Jet A, containing an antimisting polymeric additive, FM-9. A few measurements were also made on solutions of FM-9 in a mixed solvent of mineral oil, Tetralin, and o-terphenyl. Two samples of FM-9 had approximate number-average molecular weights of 12,000,000 and 8,100,000 as deduced from analysis of the measurements. The ranges of variables were 2.42 to 4.03 g/l in concentration (0.3 to 0.5% by weight), 1° to 35° in temperature, 1.3 to 9.4 cp in solvent viscosity, and 103 to 6100 Hz in frequency. Measurements in the Jet A solvent were made both with and without a modifying carrier. The results were compared with the Zimm theory and the viscoelastic behavior was found to resemble rather closely that of ordinary non-polar polymers in Θ solvents. The relation of the results to the antithixotropic behavior of such solutions at high shear rates is discussed in terms of intra-molecular and intermolecular interactions.

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INTRODUCTION

Under the above Contract, an investigation was undertaken of measurements of linear viscoelastic properties of a kerosene jet fuel, Jet A, containing an antimisting polymeric additive, FM-9. This material has very unusual rheological properties;[1] in particular, its viscosity increases sharply above a critical shear rate following a short induction time, and eventually forms a gel, which can revert to its original consistency after the shearing ceases ("antithixotropic" behavior). It was planned to study the storage and loss shear moduli in small oscillating deformations, by the multiple-lumped resonator apparatus, as a function of frequency, temperature, concentration, and presence of a "carrier"; to interpret the results in terms of current molecular theories; and to correlate the results, if possible, with the shear-thickening or antithixotropic behavior observed by Peng and Landel.[1] The personnel consisted of John D. Ferry, Principal Investigator, and Søren Hvidt, Research Assistant. The contract duration was from February 22, 1982 to September 30, 1982.

MATERIALS

Solutions of two samples of polymer FM-9, designated 1 and 2, were obtained from Drs. R. F. Landel and S. T. J. Peng, Jet Propulsion Laboratory. They appeared to be nearly identical but the polymer in 2 evidently had a slightly lower molecular weight. Polymer 1 was furnished in the usual jet fuel kerosene, "Jet A", at a concentration of 0.3% (2.42 g/l); polymer 2 was furnished in this solvent at 1% concentration and also in a mineral oil mixture. The volume concentrations refer to a temperature of 20°C. In every case, these were solutions with and without 0.6% of a modifying "carrier", which is used in practice to facilitate mixing the polymer with the fuel and is a mixture of a low molecular weight glycol and an amine. The kerosene fuel solvent with and without carrier was also furnished to enable dilutions to be made. Dilutions were made by weight.

The intrinsic viscosity $[\eta]$ of polymer 1 in jet fuel kerosene without carrier was measured at 20°C. in a Cannon-Fenske H-50 single-bulb viscometer after tests with a four-bulb viscometer gave assurance that the shear rate dependence of viscosity would not be significant under the conditions used. The extrapolated value of $[\eta]$ was 123 ml/g.

The viscosities, η_s, and densities, ρ, of the solvents were as follows:

Solvent	Temperature	η_s,cp.	ρ,g/ml
Jet A	1°C	2.56	0.819
	20°	1.68	0.806
	35°	1.30	0.797
Mineral oil mixture[a]	20°	9.44	0.952

[a] This solvent was composed of 46.2% Tetralin, 28.4% o-terphenyl, and 25.4% of a heavy grade white oil.

METHODS

The storage and loss shear moduli of all solutions were measured in small oscillating deformations by the Birnboim-Schrag multiple-lumped resonator[2] equipped with a new computerized data acquisition and processing system.[3,4] Each solution was measured at 5 nominal frequencies of 103, 420, 1030, 2530, and 6100 Hz, although in some cases the highest frequency was not reliable. Solvent without carrier was used for calibrations.

In one case, for Polymer 1 in Jet A with carrier at 20° C. and concentration 4.03 g/l, G' and G" were measured at 420 Hz over a 7-fold range of driving current, to which the shear amplitude is proportional, to determine whether this material with such unusual rheological properties would exhibit any nonlinear behavior. The values were strictly independent of amplitude, and gave assurance that the viscoelastic properties measured at the low strains provided by this instrument are linear. (The maximum shear rate at the surface of the oscillating resonator can be as high as several hundred sec^{-1} at the highest frequency of about 6100 Hz,[2,5] but falls off rapidly with increasing distance from the surface. In steady flow, such a shear rate would be somewhat less than those at which antithixotropic behavior has been observed.[1] However, its influence is expected to be far smaller in oscillating deformations than in steady flow. The maximum shear magnitude at the surface of the resonator is of the order of 0.02 or less, which represents a very small strain; also, the period of oscillation is very much smaller than the induction period required in steady flow for the onset of antithixotropy.)

Comparison of dilute-solution viscoelastic data with theory is usually based on extrapolation to infinite dilution by plotting[6] $(G'/cRT)^{1/2}$ and $(G'' - \omega\eta_s)/cRT$ against c, where ω is radian frequency (2π times the frequency ν in Hz) and c the polymer concentration in g/ml; $\omega\eta_s$ is the contribution of solvent to the loss modulus. In one case, for Polymer 2 in Jet A with carrier at 20° C., a series of dilutions was measured and the results were extrapolated to zero concentration in this way. These plots were linear; their intercepts are $[G']/RT$ and $[G'']/RT$ respectively, where $[G']$ and $[G'']$ are the limiting values of G'/c and $(G'' - \omega\eta_s)/c$ respectively as c approaches 0. However, most of the data here are reported at finite concentrations, simply as G' and $G'' - \omega\eta_s$.

RESULTS

<u>Extrapolation to Infinite Dilution.</u> The data extrapolated to infinite dilution for Polymer 2 in Jet A solvent with carrier at 20° are listed in the Appendix and plotted logarithmically against $\omega\eta_s/RT$ in Figure 1. Their frequency dependences resemble those predicted by the Zimm theory[7,8] for a flexible polymer coil molecule in a Θ solvent -- i.e., with a dominant hydrodynamic interaction parameter $h^* = 0.25$.[8] An absolute comparison cannot be made, since the

theory predicts $[G']M/RT$ and $[G'']M/RT$ as functions of $\omega\tau_1$ or $\omega[\eta]\eta_s M/S_1 RT$, where τ_1 is the longest configurational relaxation time, M is molecular weight, and the numerical factor S_1 is 2.37; in this case M and an independent determination of $[\eta]$ are not available. However, the experimental data can be matched to theoretical Zimm curves by arbitrary shifts on the logarithmic scales and in the course of this process M, τ_1, and $[\eta]$ are determined. The cross in the figure corresponds to coordinate values where $\omega\tau_1 = 1$ and $[G']M/RT$ or $[G'']M/RT = 1$. A moderately good fit is obtained with $M = 8{,}100{,}000$, $\tau = 2.9 \times 10^{-4}$ sec., and $[\eta] = 121$ ml/g.

It must be recognized that the polymer probably has a broad molecular weight distribution and the theoretical Zimm curves drawn correspond only to uniform molecular weight. However, by analogy with calculations of the Rouse theory for most probable molecular weight distribution,[9] it can be expected that the effect of distribution in this range of reduced frequency, especially on $[G'']$, will be relatively small. Much larger effects would appear at lower frequencies, and the deviation of $[G']$ at the lowest measured frequency is probably due to molecular weight distribution. The values of M and τ_1 deduced from the fit are then number-average values.[9]

It may be concluded that the viscoelastic properties in very small strains appear to be perfectly normal for a flexible coiled molecule and that the hydrodynamic interaction in this solvent with carrier corresponds approximately to a Θ solvent.

Data at Finite Concentration; Dependence on Temperature and Presence of Carrier. A larger number of measurements were made at the finite concentrations of polymer in the solutions as furnished. The data are reported as G' and $G'' - \omega\eta_s$ in the Appendix. In Figure 2, G'/cRT and $(G'' - \omega\eta_s)/cRT$ are plotted logarithmically against $\omega\eta_s/RT$ for Polymer 1 at 2.42 g/l and 20° C with and without carrier. Although strictly the Zimm theory does not apply at finite concentration, the product $c[\eta]$ here is only about 0.3 so the effects of intermolecular interaction should be moderate. In fact, the theoretical curves can be matched rather well with $h^* = 0.25$ although a slightly better fit is obtained without carrier with $h^* = 0.30$, which for infinite dilution would correspond to a solvent slightly poorer than Θ conditions. In this case of finite concentration, the horizontal and vertical shifts to match the logarithmic scales provide an apparent molecular weight M_a and longest relaxation time τ_{1a}, which without carrier are 12,000,000 and 6.0×10^{-4} sec. respectively, both no doubt a little higher than the values would be at infinite dilution. With carrier, τ_{1a} is increased to 11×10^{-4} sec., indicating an expansion of the molecules. The corresponding data at 1° C are shown in Figure 3. The behavior is similar although the fit to the Zimm theory is not so good without carrier (this is the worst fit of the approximately 20 runs made in this study). The apparent molecular weights are the same. The comparison with and without carrier is similar except that the higher solvent viscosity at 1° gives higher relaxation times. A complete list of relaxation times is given in the following section.

Dependence of Apparent Relaxation Times on Temperature, Concentration, Molecular Weight, Presence of Carrier, and Solvent. Fits of a large number of frequency dependence data on both Polymers 1 and 2 to the Zimm theory with $h^* = 0.25$ gave reproducible values of the apparent molecular weight -- 12,000,000 for Polymer 1; 9,000,000 ± 10% for Polymer 2. The latter is, as expected, slightly higher than that obtained by extrapolation to infinite dilution, 8,100,000. Again, these probably represent something close to a number-average. The logarithms of the apparent longest relaxation times are listed in Table 1. These have been *reduced* to the viscosity of jet fuel A at 20° C. by multiplication by $\eta_{s0}T/293\eta$, where η_s is the solvent viscosity at the temperature measured (T) and η_{s0} is that of Jet A at 20°. There is considerable evidence[10] that τ_1 is proportional to η_s at low concentrations, so the differences observed will be independent of the effect on viscosity of changing temperature or solvent (comparison of Jet A with mineral oil mixture).

TABLE [illegible]

Apparent Longest Relaxation Times

from Zimm Theory Fits to Frequency Dependence

Polymer	Solvent	Conc. g/l	Temp. °C	Carrier	log τ_{1a}*
1	Jet A	2.42	1	No	-3.39
			1	Yes	-2.85
			20	No	-3.22
			20	Yes	-2.96
			35	No	-3.19
			35	Yes	-2.92
2	Jet A	Extrap.	20	Yes	-3.54^x
		2.42	1	No	-3.47
			1	Yes	-3.36
			20	No	-3.56
			20	Yes	-3.24
		4.03	1	No	-3.44
			1	Yes	-3.30
			20	No	-3.33
		5.22	20	Yes	-3.26
	M.O.+	3.12	20	No	-3.18
			20	Yes	-3.09

*Reduced to the viscosity of Jet A at 20° as explained in the text.

^{x}This is τ_1, not τ_{1a}.

+Mineral oil mixture.

The influence of carrier is always to increase the relaxation time, though the degree is somewhat erratic, ranging from 20 to 100%. The influence of concentration can be seen in the two concentrations of Polymer 2 in Jet A as a moderate increase (with one exception), as expected from well-known results on normal flexible polymers.[11] The influence of temperature (after reduction for differences in solvent viscosity) is, with two exceptions, a slight increase with increasing temperature. The influence of molecular weight, in comparing Polymers 1 and 2, is seen to be an increase in τ_{1a} with M_a; it is somewhat erratic but roughly what would be expected from the difference between the two M_a values; according to the Zimm theory, τ_1 should be proportional to $M^{3/2}$. The influence of solvent is seen in the comparison of mineral oil mixture with Jet A (withrough interpolation between concentrations); even after reduction for the higher viscosity of the mixed solvent, the relaxation times are considerably higher in that solvent.

For a given molecular weight and solvent viscosity, the longest relaxation time at infinite dilution is proportional to the intrinsic viscosity, and if departures from Θ conditions are small the intrinsic viscosity reflects the average dimensions of a flexible coil. Even at small finite concentrations, the differences in apparent longest relaxation times in Table 1 can be interpreted qualitatively in terms of differences in average coil dimensions associated with solvent power. Thus, it appears that the mineral oil mixture is a somewhat better solvent than Jet A though not better enough to cause a significant departure from the Zimm theory for Θ conditions. The slight effect of increasing temperature is also consistent with an increase in solvent power. Finally, the presence of carrier evidently always causes an increase in coil dimensions.

DISCUSSION

Probably the most striking feature of these results is the normal behavior of the dilute solutions in small oscillating deformations, in contrast to the bizarre behavior at high steady-flow shear rates; they resemble solutions of an ordinary non-polar polymer in a Θ solvent. Nevertheless, it may be expected that there are some strong intramolecular interactions within a polymer molecule. Although the composition of FM-9 is not known, similar antithixotropic behavior at high shear rates has been reported[1,12] for solutions of copolymers of methyl methacrylate and methacrylic acid in ethylene dichloride. Association between carboxyl groups in a non-polar solvent would be expected to contract the molecule somewhat. By analogy, it may be inferred that the apparent nearly Θ-like behavior of FM-9 solutions is a balance between normal behavior of a non-polar polymer in a somewhat good solvent and some specific intramolecular attractive interactions. Thus, presence of the carrier, which if it is an amine would be expected to interact with carboxyl groups and decrease their binary associations, may give a more nearly normal solution. A hint of this is seen in Figure 2a.

It has been suggested[1] that the shear thickening at high shear rates is caused by disruption of intramolecular associations as the molecules are extended, followed by formation of intermolecular associations as the originally limited zone of intermolecular overlap, gauged by the value of about 0.3 for the product $c[\eta]$, is increased by molecular extension. The apparent longest viscoelastic relaxation time, τ_{1a}, is a measure of the time required for a breathing-like configurational motion in which the ends of a molecule move apart. In ordinary non-polar polymers that exhibit shear-thinning rather than shear thickening, the shear rate for onset of significant non-Newtonian behavior of this sort is of the order of τ_1^{-1}.[13] It is striking that a similar correlation exists between τ_{1a} and the critical shear rate γ_c for onset of gelation in the FM-9 solutions, measured by Peng and Landel,[1] as shown in Table II.

TABLE II

Comparison of Reciprocal Critical Shear Rates for Onset of Gelation and Apparent Longest Viscoelastic Relaxation Times, Concentration 0.3% (2.42 g/l)

	$\dot{\gamma}_c^{-1}$, sec.	τ_{1a}, Polymer 1 sec.	τ_{1a}, Polymer 2 sec.
Without Carrier	8.3×10^{-4}	6.0×10^{-4}	2.7×10^{-4}
With Carrier	3.2×10^{-4}	10.9×10^{-4}	5.7×10^{-4}

Here the $\dot{\gamma}_c$ values were measured[1] at 23.9° C and the τ's at 20.0, but the temperature difference is not important. It is not clear whether the polymer studied by Peng and Landel resembles more Polymer 1 or Polymer 2, but the times are all similar in magnitude.

Nevertheless, the correlation between $\dot{\gamma}_c^{-1}$ and τ_{1a} is not simple; presence of carrier increases τ_{1a}, but decreases $\dot{\gamma}_c^{-1}$, i.e., carrier makes it necessary to go to higher shear rates to induce gelation. Thus the effect of carrier on gelation arises from its influence on both the postulated intermolecular interactions and those intramolecular interactions which are important in small-deformation viscoelastic properties. To understand this behavior, it will probably be necessary to evaluate the kinetics of both formation and dissociation of the postulated binary associations, both intramolecular and intermolecular.

CONCLUSIONS

The linear viscoleastic behavior of solutions of the polymeric additive FM-9 in the jet fuel Jet A, both with and without a modifying carrier, as well as in a mineral oil mixture as solvent, resembles that of ordinary non-polar polymers in Θ solvents and can be described by the Zimm theory. There is no evidence of antithixotropic behavior in small oscillating deformations. Match of data to theory provides values of the number-average maximum relaxation time as a function of temperature, concentration, and presence or absence of carrier, as well as an estimate of the number-average molecular weight. The data are consistent with the presence of strong intramolecular interactions that cause the molecules in dilute solution to be somewhat more compact than would otherwise be the case in a good solvent; these interactions are diminished by presence of carrier. When the molecules are extended by high shear rates in steady flow, intermolecular interactions evidently develop and cause increase in viscosity and eventual gelation.

RECOMMENDATIONS

We make no specific recommendations. In order to understand better the nature of the postulated interactions, further work would be of value, especially if performed on materials of well-characterized composition and narrow molecular weight distribution. Investigation of superposed steady and oscillatory flow would probably be particularly instructive.

ACKNOWLEDGMENTS

We are indebted to Dr. R. F. Landel and Dr. S. T. J. Peng of the Jet Propulsion Laboratory for furnishing the materials and for frequent consultation and advice. Additional support for this work, besides the JPL Contract, was provided by the Department of Chemistry, University of Wisconsin, and Grant DMR 78-16954 from the Polymers Program, National Science Foundation. Some exploratory measurements on another FM-9 solution were made in 1975, long before the Contract, by Dr. R. W. Rosser and Dr. R. F. Landel.

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Legends for Figures

Fig. 1. Intrinsic reduced moduli $[G']/RT$ and $[G'']/RT$ plotted logarithmically against reduced frequency $\omega\eta_s/RT$ for polymer 2 in jet fuel A at 20° C with carrier. Curves drawn for Zimm theory with $h^* = 0.25$. At cross, ordinate is $-\log M$ and abscissa is $\log \eta_s/RT - \log \tau_1$.

Fig. 2. Reduced moduli G'/cRT and $(G'' - \omega\eta_s)/cRT$ at 2.42 g/l plotted logarithmically against reduced frequency $\omega\eta_s/RT$ for polymer 1 in jet fuel A at 20° C. a, without carrier; b, with carrier. Curves drawn for Zimm theory with $h^* = 0.25$ (solid) and $h^* = 0.30$ (dashed). At cross, ordinate is $-\log M_a$ and abscissa is $\log \eta_s/RT - \log \tau_{1a}$.

Fig. 3. Reduced moduli G'/cRT and $(G'' - \omega\eta_s)/cRT$ at 2.42 g/l plotted logarithmically against reduced frequency $\omega\eta_s/RT$ for polymer 1 in jet fuel A at 1° C. a, without carrier; b, with carrier. Curves drawn for Zimm theory with $h^* = 0.25$. Location of cross same as in Fig. 2.

Figure 1

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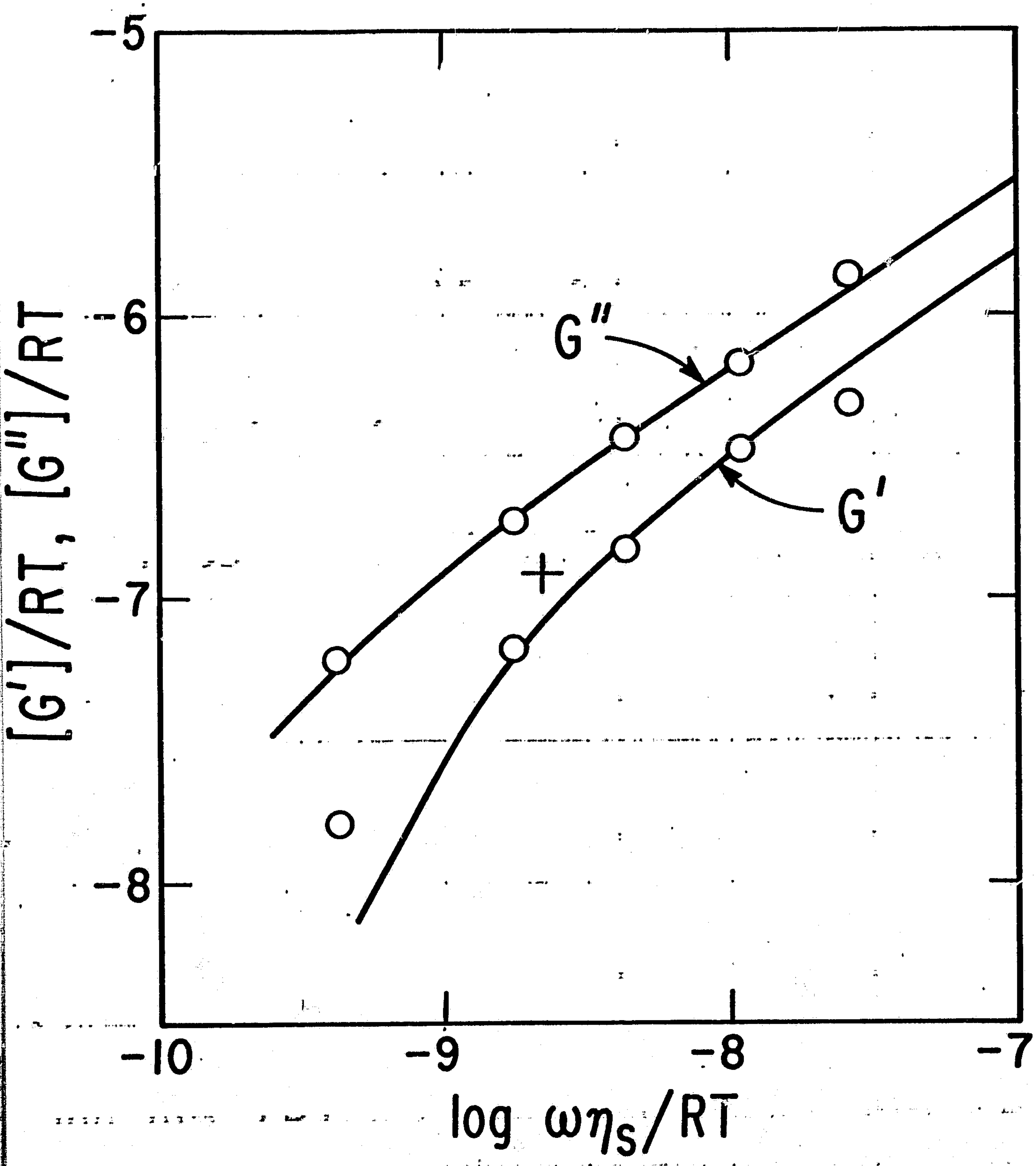

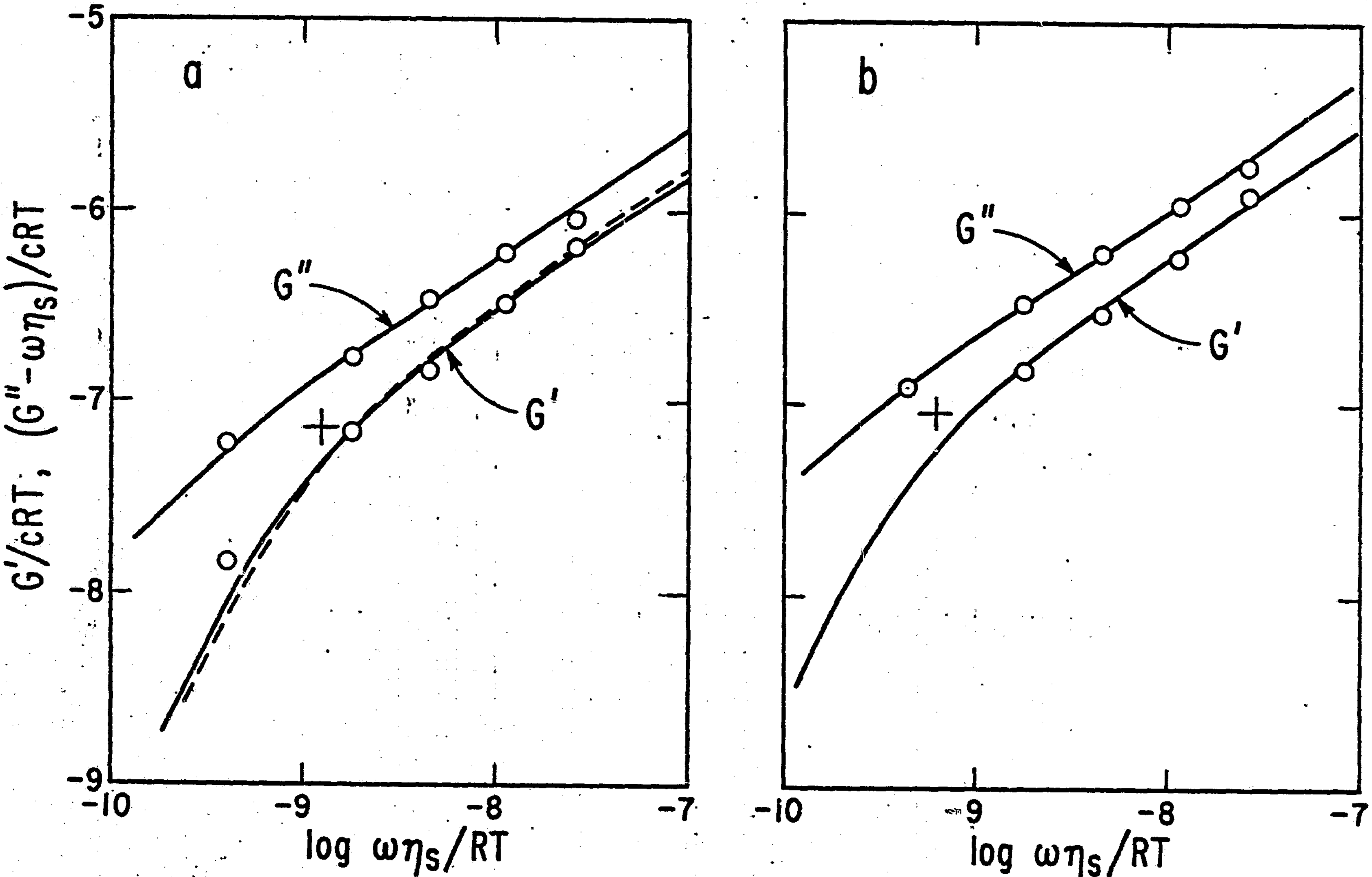

Figure 2

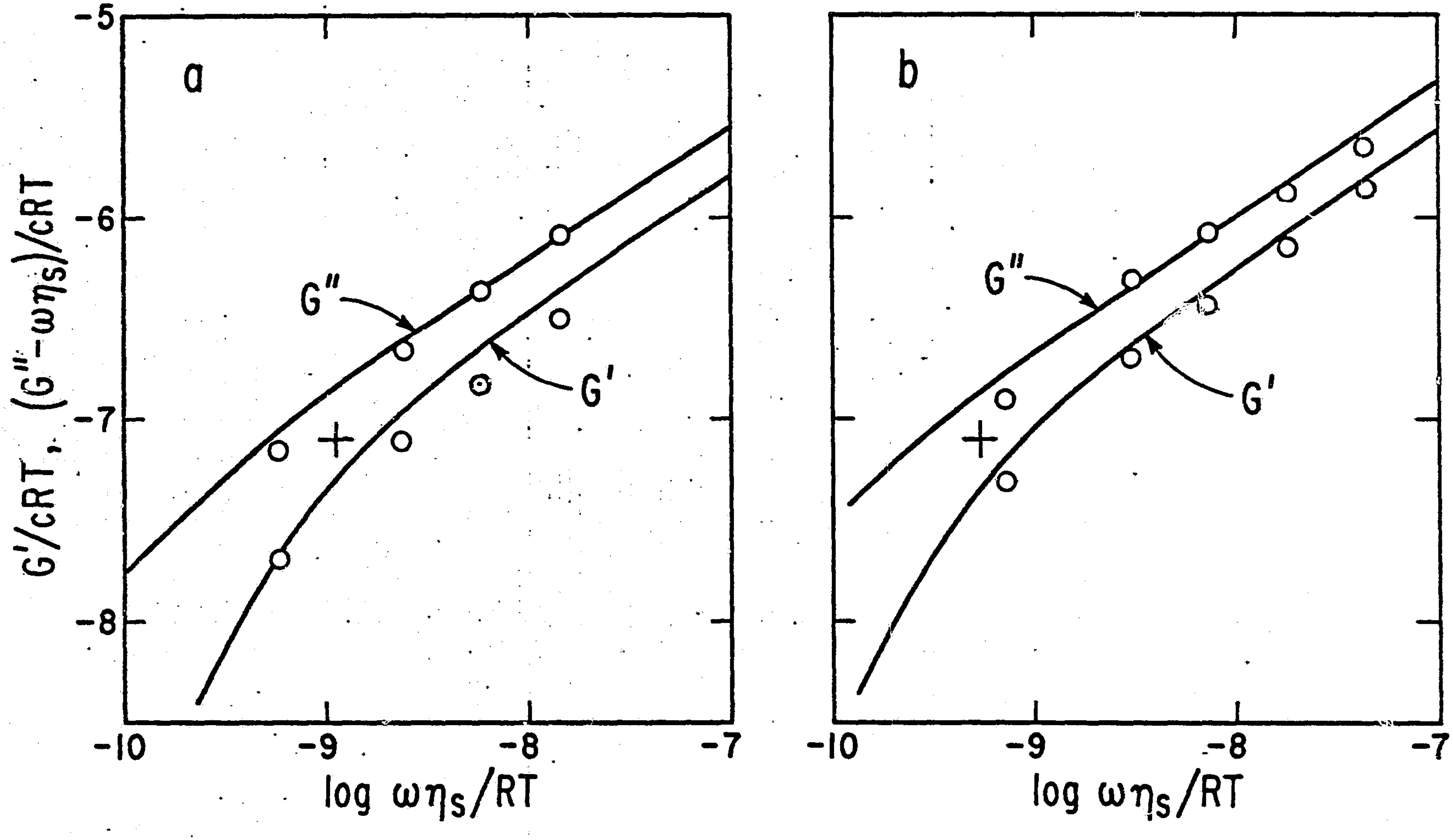

Figure 3

APPENDIX: Numerical Data

G' and G" in dyn/cm^2

A. Extrapolated Data for Polymer 2 in Jet A at 20° C. with Carrier

Freq. Hz	log [G']/RT	log [G"]/RT
104	-7.80	-7.22
419	-7.18	-6.73
1028	-6.83	-6.44
2510	-6.48	-6.17
6057	-6.31	-5.97

B. Data at Finite Concentration of 2.42 g/l for Polymer 1 in Jet A

Temp. °C.	Carrier	Run No.	ν Hz	log G'	log (G" - $\omega\eta_s$)
1	No	2540	104	0.05	0.58
			420	0.62	1.07
			1032	0.91	1.38
			2521	1.24	1.66
			6085	1.88	0.29
1	Yes	2541	104	0.44	0.95
			420	1.03	1.43
			1032	1.31	1.67
			2521	1.60	1.95
			6085	1.99	2.08
20	No	2538	103	-0.07	0.55
			418	0.61	1.00
			1027	0.93	1.30
			2508	1.29	1.55
			6054	1.73	1.59
20	Yes	2539	103	0.33	0.86
			418	0.95	1.30
			1027	1.25	1.57
			2508	1.55	1.83
			6053	1.88	2.03
35	No	2543	103	-0.10	0.56
			416	0.63	1.00
			1022	0.97	1.29
			2498	1.29	1.55
			6028	1.23	1.91
35	Yes	2544	103	0.23	0.83
			416	0.91	1.28
			1022	1.24	1.55
			2498	1.53	1.79
			6027	1.60	2.12

C. Data at Finite Concentrations for Polymer 2 in Jet A

Concen. g/l	Temp. °C.	Carrier	Run No.	ν Hz	log G'	log $(G' - \omega\eta_s)$
2.42	1	No	2636	104	0.08	0.67
				420	0.67	1.15
				1032	1.02	1.44
				2521	1.35	1.73
				6085	1.85	1.89
	1	Yes	2637	104	0.26	0.76
				420	0.84	1.23
				1032	1.15	1.51
				2521	1.46	1.81
				6085	1.69	2.15
	20	No	2632	103	-0.15	0.49
				418	0.51	0.96
				1027	0.85	1.25
				2508	1.16	1.54
				6054	1.49	1.81
	20	Yes	2627	103	0.19	0.72
				418	0.84	1.18
				1027	1.14	1.45
				2508	1.37	1.69
				6054	1.42	1.94
4.03	1	No	2634	103	0.42	0.93
				420	0.97	1.40
				1032	1.29	1.69
				2521	1.57	1.97
				6085	1.86	2.24
	1	Yes	2638	103	0.63	1.04
				420	1.15	1.48
				1032	1.44	1.74
				2521	1.73	1.20
				6085	1.96	2.28
	20	No	2633	103	0.35	0.86
				418	0.93	1.32
				1027	1.25	1.59
				2508	1.54	1.86
				6054	1.84	2.11
5.22	20	Yes	2623	103	0.83	1.19
				418	1.41	1.65
				1027	1.61	1.65
				2508	1.82	2.06
				6053	1.92	2.35

D. Data at Finite Concentration of 3,12 g/ℓ

for Polymer 2 in Mineral Oil Mixture

Temp. °C.	Carrier	Run No.	ν Hz	log G'	log $(G'' - \omega\eta_s)$
20	No	2630	102	1,19	1.47
			416	1,63	1.87
			1025	1,89	2.12
			2505	2,14	2.39
			6049	2,46	2.64
	Yes	2631	102	1,26	1,52
			416	1,69	1,90
			1025	1.95	2.14
			2505	2.19	2,40
			6049	2.43	2.70