EFFECT OF CROSSLINK DENSITY ON THE

CREEP BEHAVIOR OF NATURAL RUBBER VULCANIZATES[a]

Donald J. Plazek

Mellon Institute
Pittsburgh, Pa. 15213

[a] This paper was presented at the 36th Annual Meeting of the Society of
Rheology which was held at Case Institute of Technology, Cleveland,
Ohio, October 25-27, 1965.

ABSTRACT

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Torsional creep measurements on four natural rubber vulcanizates, crosslinked to different degrees, were carried out in the temperature range -50°C to 90°C. This investigation complements the studies on identical samples of the stress relaxation behavior by Chasset and Thirion and of the dynamic mechanical response by Ferry, Mancke, Maekawa, Oyanagi, and Dickie. The creep measurements being reported are shown to be in agreement with the stress relaxation results. In addition to the usual temperature reduction, a superposed curve was obtained using the apparent molecular weight between crosslinks, M_c, as a reduction variable. The variation in viscoelastic response with crosslink density is interpreted as a restrictive action of the chemical crosslinks on the transient entanglement network.

INTRODUCTION

The viscoelastic behavior of crosslinked elastomers in the transition from glasslike to rubberlike behavior has been frequently studied,[1-5] and a number of the investigations have extended well into the rubbery region of response.[6-10] In this latter region the lack of equilibrium behavior of polymer networks has been observed as continuing stress decay at constant strain or increasing deformation under constant load. Under sinusoidal deformation a low but persistent loss is observed even at the lowest frequencies of measurement. However, little progress has been made in establishing the systematic phenomenological patterns of behavior which are characteristic of these materials at long times, much less in understanding the molecular processes responsible for the lack of time-independent response.

Recently a series of natural rubber samples crosslinked to various degrees was prepared in the laboratory of Dr. Pierre Thirion, Institut Francais du Caoutchouc, Paris. Careful stress relaxation measurements on this series made by Chasset and Thirion[11] clearly showed that the degree of crosslinking is the dominating variable for the response in the long time domain. A study was first made[12] at temperatures between 65° and 100°C where thermal degradation is the principal contributor to stress decay after the first day or two following the application of strain to the rubber. With the resulting information on the kinetics of degradation it was possible to predict the onset of a measurable contribution by degradation to the relaxation. Measurements were confined to times where the

response was entirely viscoelastic in the subsequent study.

Identical samples at five different crosslinking levels were sent to the laboratory of Professor John D. Ferry, University of Wisconsin, Madison, where R. G. Mancke, E. Maekawa, Y. Ōyanagi and R. A. Dickie[13] assisted in characterizing the dynamic mechanical properties in the region of time scale extending from the glasslike to rubberlike transition to that covered by the stress relaxation measurements.

Shear creep compliance, $J(t)$, results are being reported here on four samples of this natural rubber series that have generously been provided to us by Dr. Thirion. These complementary results encompass the entire range of reduced time covered in the other two investigations and help give a unified picture of the effect of crosslinking on the viscoelastic response of crosslinked polymers.

EXPERIMENTAL

The natural rubber, NR, samples were prepared from smoked sheet rubber that had a low content of inorganic impurities. 3.5% of the cross-linking agent, dicumyl peroxide (DCP) was used and the vulcanization time at 135°C was varied to obtain the different degrees of crosslinking, see Table I. The equilibrium swelling in benzene at room temperature was determined to insure that our samples had not changed since their preparation. Using the values of the volume fraction of rubber in the swollen samples,

v_2, in the Flory-Rehner equation,[14] $M_c = \dfrac{\rho V_o (v_2^{1/3} - \frac{1}{2} v_2)}{-\ell n(1-v_2) - v_2 - \mu v_2^2}$, the

apparent effective molecular weight between crosslinks, M_c, was calculated. V_o is the solvent molar volume, ρ is the density of the dry rubber and $\mu = 0.444$ is the natural rubber-benzene polymer-solvent interaction coefficient determined by Chasset and Thirion. Densities were determined by means of flotation in ethanol-water mixtures and cubic thermal expansion coefficients, α, from length measurements with a traveling microscope. The results for α on the NR samples scattered between 6.2 and $5.7 \times 10^{-4} \, °C^{-1}$ and an average of 6.0×10^{-4} was used. The values of ρ and v_2 are given in Table I along with the resultant M_c's, which agree within experimental error with those reported by Thirion and Chasset.[11] The swelling medium was reagent grade thiophene-free benzene (J. T. Baker Chemical Co., Phillipsburg, N. J.).

Table I

Characteristics of the Rubber Vulcanizates

Vulcanizate	Curing time (min.)	$\rho(30°)$ g/cm^3	v_2 [a]	Sol fraction $\times$ 100	M_c [b]	M_c [c]
F	20	0.9086	0.129$_1$	4.6	20,500	20,000
G	30	---	---	---	---	14,800
H	40	0.9086	0.167$_3$	3.6	11,200	11,400
I	75	0.9092	0.196$_1$	3.3	7,400	7,600
J	150	0.9099	0.224$_1$	3.0	5,200	5,400

a, swelling medium is benzene; b, from swelling in this study; c, from swelling ref. 11.

Most of the shear creep compliance results being reported were
obtained using a torsion instrument[15] with a rotor which floated in an
extremely low vapor pressure liquid (tri-m-tolyl phosphate). Measurements
on the rubbers were made both with the original torque-producing device,
a modified pair of wattmeter drive units, and with a later-developed drag
cup motor for precise torque production. The field coils of the motor
produce a rotating magnetic field which induces a drag torque on an
essentially static aluminum cup that resides in an annulus air gap. The
same kind of motor is used in the other creep instrument used in this study.
In this latter instrument a magnetic bearing is used to support the rotor
and the sample atmosphere can be controlled. In addition to checking
many of the measurements made in the float instrument this second apparatus,
with its wider temperature range, was used to obtain results at temperatures
down to -50°C. The specimens measured were right circular cylinders about
0.4 cm. in diameter and 0.5 cm. high. Maximum strains of about 1% were
experienced by the specimens.

RESULTS

The four natural rubber samples F, H, I, and J were each

measured in the float torsional creep apparatus at 5 or 6 temperatures

in the range 0° to 90°C. Most of the shear creep compliance curves,

$J(t)$, cm^2/dyne, obtained on samples F and I are presented logarithmically

in Fig. 1 as a function of logarithmic time (where the time is expressed

in seconds). $J_p(t) = J(t)\frac{T\rho}{T_o\rho_o}$, where T is the absolute temperature,

has been plotted to account for the entropic nature of the response.[16]

Note change in scale F to I. Several of the problems encountered in

the investigation are illustrated in these data.

The effect of crystallization during a creep run an be easily

seen in the 1°C curve of sample F as positive curvature following the point of

inflection at log t = 4.5. Such an increase in the derivative d log $J(t)$/d log t

need not necessarily reflect additional crystallization occurring during the creep

run but could indicate concurrent thermal degradation or the onset of an actual

additional viscoelastic dispersion. However, since the melting point,

T_m, of natural rubber is 28°C,[17] and since its depression by moderate

crosslinking is slight[18] it was realized that some crystallization might

occur at the lower temperatures of measurement. Below 30°C noticeable

thermal degradation does not occur during periods of one to 10 hours,[12]

so an isothermal drop in the compliance curve with time was concluded to

indicate a growing degree of crystallinity. The compliance decrease was

measured either by carrying out successive short creep runs (10 seconds)

with the sample otherwise in an unloaded condition, or by removing the

torque periodically for 10 seconds during a prolonged creep run. Such

intermittent checks do not affect the creep response measurably for
longer than a few minutes, and were also used after the first hour of
creep at higher temperatures to detect the presence of thermal degradation.
Since the rate of creep was small for most of the measurements following
shorter runs, the first 10 seconds of the recovery provide an identical
check on the level of response. Check runs at 30°C preceding and
following most measurements were also used to keep track of the sample
stability. In spite of the enhancement of the deformation caused by the
occurrence of crystallization, the compliance level, as measured by the
recovery portion of the run and a subsequent short check run, fell an
appreciable 16% during the 3-day run. The enhancement suggests that
even at the low stress imposed on the sample (2×10^4 dynes/cm^2 maximum)
the orientation of the chains in the crystallites formed was biased in
the direction of the applied stress. Subsequent heating above the melting
point restored the original compliance level, thereby confirming the above
conclusions. Since we found, in agreement with previous work,[19,20] that
the compliance decrease caused by the early stages of crystallization
is linear in time, a one percent change was present after the sample was
at temperature for three hours. One can therefore confidently accept
the results up to 10^4 seconds at 1°C. The rate of crystallization diminishes
appreciably with increasing crosslinking,[18] so other members of the NR
series are less affected.

Checks during and after the 3-day run at 30°C indicated a one
percent decrease in compliance by the end of the run. Nothing was observed
in the rest of our measurements to indicate an additional viscoelastic

dispersion in this region and four other samples[a] consistently yielded

an increase in compliance level during and after measurement when degradation

occurred at the higher temperatures, 40 to 90°C. We are left with the

conclusion that the abrupt increase in $d^2 \log J(t)/d \log t^2$ at 30°C was

caused by a slight amount of crystallization which was induced by the

applied stress.

Since for the NR samples thermal degradation inevitably led to

an increase in compliance level, reflecting a decrease in the concentration

of effective network chains, it can be concluded that the free radicals

formed upon chain scission were terminated and became loose-ended chains.

Our measurements were carried out in air. Since similar measurements

by Gent[21] which focused on the degradation-enhanced creep (secondary creep)

showed a marked decrease in the secondary creep when carried out in vacuum,

it is reasonable that the free radicals react with oxygen. The 40 and 60°

curves for I, shown in Figure 1 show an appreciable secondary creep contri-

bution to the measured compliance beyond $\log t = 3$.

The very small slopes exhibited by the $\log J_p(t)$ curves compli-

cated the reduction procedure slightly. Relatively small errors in sample

coefficient or instrument parameter values can cause enormous errors in

the temperature shift factor, a_T,[22] or make reduction completely impossible.

We have therefore matched the curvature of runs at different temperatures

to achieve reduction and allowed ourselves the freedom of applying the

necessary vertical shifts to achieve superposition. The logarithms of

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[a] A fifth sample, K, was measured, but since the swelling and the creep
behavior differed very little from F the results are not being reported
here. A 20-hour creep measurement at 40°C on this vulcanizate showed
no abrupt increase in $d^2 \log J(t)/d \log t^2$ and no change in compliance
level, thereby arguing for no degradation in F at 30°C.

the a_T and empirical vertical shift factors, $\Delta \log J(T)$, used are presented

in Table II. For all of the measurements taken above 0°C the $\Delta \log J(T)$

shifts are within our ± 1 percent repeatability after a temperature cycle.

We believe our results to be accurate within about 3 percent and our

precision within a run is about 1/4 percent. In addition to thermal

degradation, occasional crystallization, sample coefficient errors, and

the uncertainty in the instrument parameters (some of which have been con-

siderably reduced since this investigation began) we believe our precision

was limited by a dependence of the shear compliance on the slight axial

compression (ca. 2%) on the sample.[23] In Figure 2 the resulting reduced

$\log J_p(t)$ curves (reference temperature, T_o = 30°C) are shown for the

samples NR-F, H, I, and J. It is clear that the degree of crosslinking

has a pronounced effect on the percentage increase of creep observed in

this region. In fact, the amount of creep exhibited by F is about 10

fold that displayed by J. The dash lines in Figure 2 were calculated

from the elongational stress relaxation results of Chasset and Thirion.

Force values divided by the unstressed sample cross-sectional areas,

$\sigma(t)$, were reported.[11,24] The derived quantity represented by the dashed

lines is $\frac{\sin m \pi}{m \pi} \left(\frac{\lambda - \lambda^{-2}}{\sigma(t)} \right)$,[25] where $m = d \log \sigma(t)/d \log t$ and λ, the

elongation ratio = 1.50. Extrapolating isochronal values of $\sigma/(\lambda-\lambda^{-2})$

from Chasset and Thirion's measurements at different elongation ratios

to λ = 1.0 an increase of 9.5 ± 1.0% is obtained. Assuming that Poisson's

ratio, μ, is 1/2, to a good degree of approximation $\lim\limits_{\lambda \to 1} \frac{\sin m \pi}{m \pi} \left(\frac{\lambda-\lambda^{-2}}{\sigma(t)} \right)$

should be equal to $J(t)$. The actual percentage differences obtained

Table II

Derived Parameters of the Rubber Vulcanizates

Vulcanizate	T°C	$\log a_T$	$\Delta \log J(t)$	$\log J_e$	$\log \dfrac{J_e(F)}{J_e(x)}$ [a]	$\log \dfrac{J_e(F)}{J_e(x)}$ [b]	$\log a_x$
F	1	1.34	0.010				
	10	0.85	0.000				
	20	0.41	0.000				
	30	0	0.000	-6.227	0	0	0
	40	-0.18	-0.004				
	60	-0.71	-0.010				
G	30	---	---	-6.357	0.130	0.132	-2.48
H	0.7	1.42	-0.004_5				
	10	0.73	-0.003				
	20	0.33	-0.003				
	30	0	0.000	-6.460	0.233	0.231	-4.15
	40	-0.32	-0.003				
	60	-0.76	0.000				
	80	-0.92	0.001				
I	1	1.20	0.0014				
	10	0.71	0.0016				
	20	0.32	0.0000				
	30	0	0.0000	-6.606	0.379	0.382	-6.76
	40	-0.24	0.0012				
	60	-0.62	0.0010				
J	-49.8	6.52	0.0115				
	-35.5	4.57	-0.0006				
	-23.7	3.40	0.0090				
	-10.4	2.20	0.0000				
	1.0	1.27	-0.0063				
	10	0.63	-0.0040				
	20	0.20	-0.0025				
	30	0	0.0000	-6.717	0.490	0.484	-9.94
	40	-0.33	0.0005				
	60	-0.70	0.0025				
	90	-1.00	0.0061				

a, this study; b, from reference 11 using extrapolated not averaged values.

between the $J_p(t)$ and $\lambda = 1.50$ curves, as seen in Fig. 2, are F, 9.1;

H, 8.6; I, 7.2, and J, 7.9%. The agreement is within the estimate of

our absolute accuracy of 3% and it is concluded that our shear creep

compliance results are in complete accord with the elongational stress

relaxation results of Chasset and Thirion. The reduced log $J_p(t)$ curves

for samples I and J are shown plotted in Fig. 3 with an appropriately

expanded ordinate scale where the degree of scatter and the contribution

of thermal degradation can be more readily assessed.

M_c reduction

It is widely acknowledged that the equilibrium response of an

elastomer is largely independent of the chemical character of the polymeric

chains making up the molecular network. The statistical mechanical theory

of rubberlike elasticity indicates that only the number of effective mole-

cular chains per cm^3 is important.[26] A small effect for dry rubbers is

to be expected if the average chain end to end distance is temperature

dependent;[27,28] and indirectly the chemical character of the polymer has an

effect on the concentration of effective chains through the determination

of the degree of entanglement present. We would like to propose here

that within a constant factor which is related to the average monomeric

friction coefficient the approach to mechanical equilibrium of an elastomer

is insensitive to its chemical character. In addition it is suggested

that the terminal region of the retardation spectrum of an elastomer has

one characteristic shape regardless of the degree of crosslinking.[†] Based

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[†] It appears reasonable that future measurements may demand that the
above statements apply only to randomly crosslinked flexible polymers.

on these propositions it should be possible to construct a universal curve

with the creep compliance data shown in Fig. 2. By applying a vertical

shift to the curves representing the response of samples H, I, and J,

which is presumed to be only a function of the equilibrium shear creep

compliance, J_e, and a horizontal shift along the time axis a reduced

curve relative to the response of the reference sample F can be con-

structed. The overlapping portions of the log $J_p(t)$ curves were found

to match in shape within experimental error. Such an empirical shifting

procedure was applied with the result being shown in Fig. 4 where

$$\log J_x(t/a_x) = \log J_e(M_c) + \log \frac{J_e(20,300)}{J_e(M_c)} + \log \psi_x(t/a_x).$$

$\psi_x(t)$ is a normalized terminal retardation function, $\lim_{t \to \infty} \psi_x(t) = 1$.

The value for $J_e(20,300)$, that for reference sample F, was taken to be

one percent greater than the final level reached by the $J_x(t)$ curve. A

linear extrapolation of the log $L_2(\tau)$, the logarithm of the second approxi-

mation to the retardation spectrum,[22,29] which is also shown in Fig. 4 yields

an additional contribution to the compliance of slightly greater than one

percent. We believe such an extrapolation results in a maximum estimate

of the remaining unobtained creep deformation. The values of the vertical

shift employed in obtaining the universal creep curve, $\log \frac{J_e(20,300)}{J_e(M_c)} \equiv$

$\log \frac{J_e(F)}{J_e(x)}$, are compared with those obtained from the mathematical extra-

polation procedure employed by Chasset and Thirion in Table II. The

excellent agreement is evidence indicating that the graphical reduction

procedure is allowable within the precision of both sets of data. The

$\log \dfrac{J_e(20,300)}{J_e(M_c)}$ values are simply subtracted from the log $J_e(20,300)$

value of -6.227 to obtain values for the samples at higher crosslinking

density. Smoothed values of log $\psi_x(t)$ are presented in Table III.

The required time axis shifts, log a_x, for superposition of the

log $J_p(t)$ curves are also given in Table II and are shown plotted against

log M_c in Fig. 5. The filled circles on the natural rubber, NR, curve

reflect values of M_c calculated from our swelling results and all the open

circles from swelling measurements of Chasset and Thirion.[11] The log a_x values

shown for the styrene-butadiene rubber, (23.5/76.5) SBR, series of samples

were obtained by converting the elongational stress relaxation results

of Chasset and Thirion[24] to shear creep compliance curves and superposing

them on the curve shown in Fig. 4. At present the meaning of the power

relationship expressed by the straight lines seen in Fig. 5 is not known,

but the fact that within experimental scatter both the NR and SBR lines

have the same slope, 15.4, is clear-cut evidence that the form of the

log $J_x(t/a_x)$ curve is the same for these rubbers of highly different

chemical structure. It is believed that the displacement of the lines

on the log a_x axis is a measure of the relative average monomeric friction

coefficient, ζ_o. Catsiff and Tobolsky[7] have compared the stress relaxation

behavior of a similar SBR rubber (25/75) to that of a natural rubber sample

and found in the region of time scale where monomeric friction coefficients

are usually calculated[22] that the SBR primary transition is located at

longer times by about 2 logarithmic decades. The displacement on the

log a_x axis of the lines in Figure 5 is approximately 3 logarithmic decades.

Table III

Smoothed Normalized Terminal Retardation Function, $\psi_x(t)$
Position on Time Scale Is That of NR-F

$\log t/a_x$	$\log \psi_x(t)$	$\log t/a_x$	$\log \psi_x(t)$
-1	-0.2315	7	-0.0355
0	-0.1906	8	-0.0277
1	-0.1578	9	-0.0214
2	-0.1286	10	-0.0163
3	-0.1039	11	-0.0122
4	-0.0821	12	-0.0086
5	-0.0606	13	-0.0058
6	-0.0472	14	-0.0040

At the present then it can be said that the enhancement of ζ_o by entanglements is roughly similar for different polymers. In addition, since many polymers have a log ζ_o at T_g in the neighborhood of 4.0^{22} the relative position of lines for rubbers of different chemical structure in Figure 5 should reflect relative values of their T_g's. Focusing on NR and SBR rubbers with the same M_c's it can be seen that log a_x for the SBR rubber is less negative. This means that the SBR rubber is creeping at a relatively greater rate, or in other words it is further from equilibrium. One would therefore conclude that its T_g is higher. A reasonable T_g for a SBR rubber with 23.5% styrene is about $-55°C^{30}$ which would place it about 20°C higher than the T_g for natural rubber. More comparisons are in order to check the propositions made here.

Extent of the terminal creep.

The above arguments make clear the need to relate the terminal creep region to the principal peak in L since only relative to it can one measure the breadth of that part of the spectrum contributing to creep in the rubbery plateau. An attempt was therefore made to obtain creep measurements on samples F and J at lower temperatures (i.e., at short equivalent times). Trouble was expected from crystallization so J, the slower crystallizing sample, was measured first. To minimize the amount of crystallization that would occur, rapid cooling past the temperature of fastest crystal growth (ca. $-20°C)^{18}$ to $-50°C$ was carried out by immersing the sample chamber of our instrument in a container of dry ice. The sequence of runs on the two samples was: J; 30.0, -49.8, -23.7, 30.0,

-35.5, -10.4, and 30.0°C: F; 30.0, -49.8, -35.5, -24.5, -10.2, and 30.0°C.
As can be seen by the small necessary vertical shifts for the runs on J,
see Table II, negligible crystallization was present throughout the
series. The temperature reduced results which extend at short times into
the beginning of the primary transition region are shown in Fig. 6. However,
it is clear from the low original positions of the low temperature curves
for sample F (the dotted lines) that some crystallization occurred during
cooling and even greater amounts while sitting near the temperature of
fastest crystallization. The positions of these curves on the time scale
were determined using the log a_T shift factors determined from the measure-
ments on J. A slight amount of error is thereby introduced since the
different degree of crosslinking necessarily means that the T_g's are
somewhat different and hence also the temperature dependences. It appears
as judged by their shapes that negligible crystallization occurred during
the 1000 second creep runs at -24.5° and -10.2°C. Furthermore, one can
conclude that the degree of crystallinity present during the runs was so
small that the form of the response was unaltered. Since the combined
runs at -49.8 and -35.5 came close to meeting the reduced curve obtained
above 0°C, only they were shifted vertically to the proper position.
The solid lines between log t/a_T = -1.0 and 5.0 are the same curves as
displayed in Fig. 2 and the dashed lines are the appropriately positioned
log $J_x(t/a_x)$ curves. It can be seen that the log $J_p(t)$ curve for J
significantly departs from the universal curve at log $t/a_T \simeq$ -2. It is
evident that the proximity of the primary transition requires such a
departure.

Temperature Dependence.

The temperature dependent shift factors, log a_T, for F, H, and J determined between 0 and 90°C are shown in Fig. 7 along with the lower temperature values for J. The universal form of the WLF equation[31]

$$\log a_T = -8.86(T-T_s)/[101.6 + T - T_s]$$

with a $T_s = -21^2$ is drawn in Fig. 7, shifted to a reference temperature of 30°C. The data fall within experimental error on the curve up to 130°C above T_g. This range is more than is usually expected, but we wish to make clear that all of the values of log a_T determined above 0°C are to be considered relatively unreliable because of the small slopes observed in the primary data.

Retardation Spectra.

The retardation spectrum, L, cm^2/dyne, for all of the reduced data was calculated using the second approximation method of Williams and Ferry, which was adapted to creep by Stern.[22,29] Several curves were also treated with Leaderman's expression[25] with a resulting excellent agreement. The retardation spectra, which reflect all of the information contained in the original data are plotted logarithmically in Fig. 8 as a function of the logarithm of the reduced retardation time, τ_r. The part of the spectrum of F that is presented covers a sizable range of 21 logarithmic decades of reduced time. The dashed line reflects the portion obtained

from the M_c reduction. The extent of the slowly diminishing spectrum

shows clearly why many attempts to reach equilibrium deformations in

elastomers have failed. To come within one percent of equilibrium in F,

assuming no chemical degradation, would take over a million years at 30°C.

Those familiar with calculations of spectra will appreciate that the

scatter is not abnormal and that within experimental error the shapes of

the spectra for H, I, and J beyond log τ_r = 0 are the same as those parts

of F to which the compliance curves of the three respectively contributed.

The apparent independence of the form of L to the degree of crosslinking

and chemical character indicates that the kinetics of the approach to

equilibrium deformation in creep or equilibrium stress in stress relaxation

is solely a function of the distance from that equilibrium.

In other reduction schemes shifts of curves along the time axis

reflect a difference in average friction coefficient in the original and

reduced states. Such is not the case with the M_c reduction. There is

certainly very little difference in the terminal region friction coefficients

of the differently crosslinked NR samples. We interpret the picture pre-

sented in Fig. 8 to indicate that the principal viscoelastic effect of

the chemical crosslinks is to eliminate retardation mechanisms arising

from non-affine motions or adjustments of the chain entanglements. The

attrition of the longest retardation mechanisms is greater resulting in

the apparent time axis shift, log a_x. Since both the chain lengths

between crosslinks and entanglements have random distributions, as the

average chain length between crosslinks approaches the average entangle-

ment length the longest chains between entanglements will be eliminated

from transient load bearing in greater numbers than short chains. If we

think of the transient entanglement network and the permanent crosslink

network as being interpenetrating, the above point becomes clear.

Parts of molecular chains that are incorporated into the per-

manent network, by having no entanglements between crosslinks, cannot

participate in the long time processes. This picture also demands that

as the crosslink density increases the entanglements are more effectively

trapped into permanent load bearing. Therefore the efficacy of an entangle-

ment should be greater than at a low crosslink density where time dependent

adjustments of the entanglement junctures will lead with greater probability

to a transfer of load to nearby chains which are fixed by permanent cross-

links. In view of the viscoelastic response observed at varying crosslink

density we cannot accept the assumption of Bueche[32] and Mullins[33] that

all of the entanglements present in the rubber precursor are equally

effective in producing load-bearing chains as are crosslinks. The fact

that Mullins deduces what appears to be an unusually high value for M_e,

the molecular weight between entanglements in the infinitely long natural

rubber precursor (14,000), is evidence that entanglements are less effec-

tive than crosslinks. Since we did not have the precursor to our natural

rubber samples, creep measurements were made on an uncrosslinked high cis

content synthetic cis-isoprene sample.[a] An M_e of 6400 was obtained from the

Andrade intercept,[34] $J_A = \frac{M_c}{\rho RT}$. Other literature values[22] obtained from

the more arbitrary points of inflection in viscoelastic curves of natural

rubber are: 5000, $G'(\omega)$; 6800, $G'(\omega)$; and 8200, $J(t)$. The above

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[a] This sample was generously supplied to us by Dr. Edward Collins of the
B. F. Goodrich Development Center, Avon Lake, Ohio.

conclusions drawn from this study agree in large part with those of

Maekawa, Mancke, and Ferry which were deduced from their study on poly-

butadiene rubbers.[36]

If the number of crosslinks introduced in an originally linear

chain sample is insufficient to produce a complete three dimensional net-

work, the resulting material is composed of highly branched chains. In

this case that part of the retardation spectrum arising from entanglement

adjustment is enhanced[37] and most probably extends to much longer times

than that of an equivalent molecular weight linear material. Therefore,

since a lightly crosslinked rubber will differ little in behavior from a

very high molecular weight branched material, except for the absence of

permanent deformation (i.e., flow), the presence of the crosslinks will

be responsible for the existence of many loss mechanisms not present in

the precursor. The elimination of mechanisms with increasing crosslinking

as described earlier will be relative to some maximum present in a nascent

molecular network.

The dotted lines in Fig. 8 represent a decomposition of the

spectrum of J into two groups of mechanisms by allowing an extrapolation

of the spectrum derived from $J_e(F)\psi_x(t)$ to short times. The resulting

fall from the maximum appears reasonable, but the ascending tendency of

the other curve clearly indicates that such an extrapolation cannot be

valid at times shorter than log τ_r < -5. A plateau to the left of the

maximum would be predicted and such does not exist.[22] This conclusion

is in accord with the statement that log a_x does not represent a difference

in molecular friction coefficient but a decrease in the number of

contributing retardation mechanisms. Although it appears not to, $\psi_x(t)$ actually changes shape as crosslinking increases; it does not actually shift on the time scale.

It can be seen in Fig. 8 that the apparent one-half logarithmic decade difference in the position of the F and J creep compliance curves (see Fig. 6) at short times, log $t/a_T < \cdot 5$, is in reality largely a difference in the heights of the primary transition peaks in L and not a difference in friction coefficient which would imply a substantial difference in free volume in the two rubbers. Less than 1/3 of the difference can be accounted for by estimating the enhancement of peak heights arising from short time entanglement mechanisms or in other words mechanism overlap. The main reason for the smaller primary transition peak of J must be that in J the average molecular weight between crosslinks, M_c (5300), is smaller than M_e (6400). More long-time, entanglement and crosslink unencumbered, normal mode chain motions are present in the response of F simply because F contains longer chains between impediments.

CONCLUSIONS

The measurements of the shear creep compliance of the NR vul-
canizates have been found to be in agreement with the elongational stress
relaxation results of Chasset and Thirion.[11] Attainment of true mechanical
equilibrium in air was not achieved and judged impossible before the inter-
vention of thermal degradation. The molecular weight between crosslinks,
M_c, has been proposed as a reduction variable. Application of the pro-
posal leads to an extended reduced curve which may be used to estimate
J_e for vulcanizates from limited creep data. The (23.5/76.5) SBR rubber
system has been shown to exhibit, within a proportionality factor the
same approach to equilibrium. The velocity of creep appears to be solely
a function of the distance from equilibrium. A phenomenological picture
of the effect of the degree of crosslinking on the viscoelastic behavior
of elastomers has been presented. The principle effects of the cross-
link density on the retardation spectrum are in the region of time scale
where in an uncrosslinked polymer the retardation mechanisms observed
are attributed to long-range coordinated motions that exist because of
molecular entanglements. A priori, there appears to be no reason to
invoke mechanisms besides the restrictive interaction of the chemical
crosslinks on the response of the transient entanglement network.

It is pointed out that when the average molecular weight between
crosslinks approaches that between entanglements the restrictive action
extends to the primary softening transition.

ACKNOWLEDGMENTS

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LEGENDS FOR FIGURES

Figure 1   The shear creep compliance, $J_p(t)$, $cm^2/dyne$, of natural rubber samples F and I plotted logarithmically against the time, sec. Temperatures of measurement indicated. Subscript p indicates amplitude adjustment for the theoretically predicted temperature dependence. Note difference in scales.

Figure 2   Logarithmic plot of $J_p(t)$ against reduced time scale, t/a_T, for samples F, H, I, and J. a_T is the time scale shift factor required for temperature reduction. Reference temperature T_o = 30°C. Dashed lines represent shear creep compliances calculated from elongational stress relaxation measurements of Chasset and Thirion at an extension ratio, λ, equal to 1.5.

Figure 3   Temperature reduced compliance curves for sample I and J presented as in Fig. 2, but with an expanded ordinate scale.

Figure 4   Logarithmic plot of $J_x(t)$, the extended compliance curve resulting from reduction using M_c as a reduction variable, versus the logarithm of the reduced time, t/a_x. $J_p(t)$ curves of samples H, I, and J have been reduced to the reference sample F. The second approximation calculation of the retardation spectrum, L_2, derived from $J_x(t)$ is also presented logarithmically.

Figure 5   Log a_x shown plotted against the logarithm of the apparent molecular weight between crosslinks, M_c, for the natural rubber, NR, and styrene-butadiene rubber, SBR series. Filled-in points from swelling measurements, this study; open points from ref. 11.

Figure 6   Temperature reduced log $J_p(t)$ curves of F and J extended to primary softening transition at shorter reduced times (log t/a_T) using lower temperature measurements as indicated. Solid lines between log t/a_T of -1 and 5 from Fig. 2. Long dashed lines are appropriately positioned log $J_x(t)$ curve. Short dashed lines indicate vertical position of lower temperature results on F as measured.

Figure 7   Logarithms of temperature shift factors a_T determined for

samples F, H, and J as function of temperature. Line
calculated from WLF equation.

Figure 8   Second approximation to retardation spectra for all samples
presented logarithmically as a function of the logarithmic
reduced retardation times; reference temperature, $T_o = 30°C$.
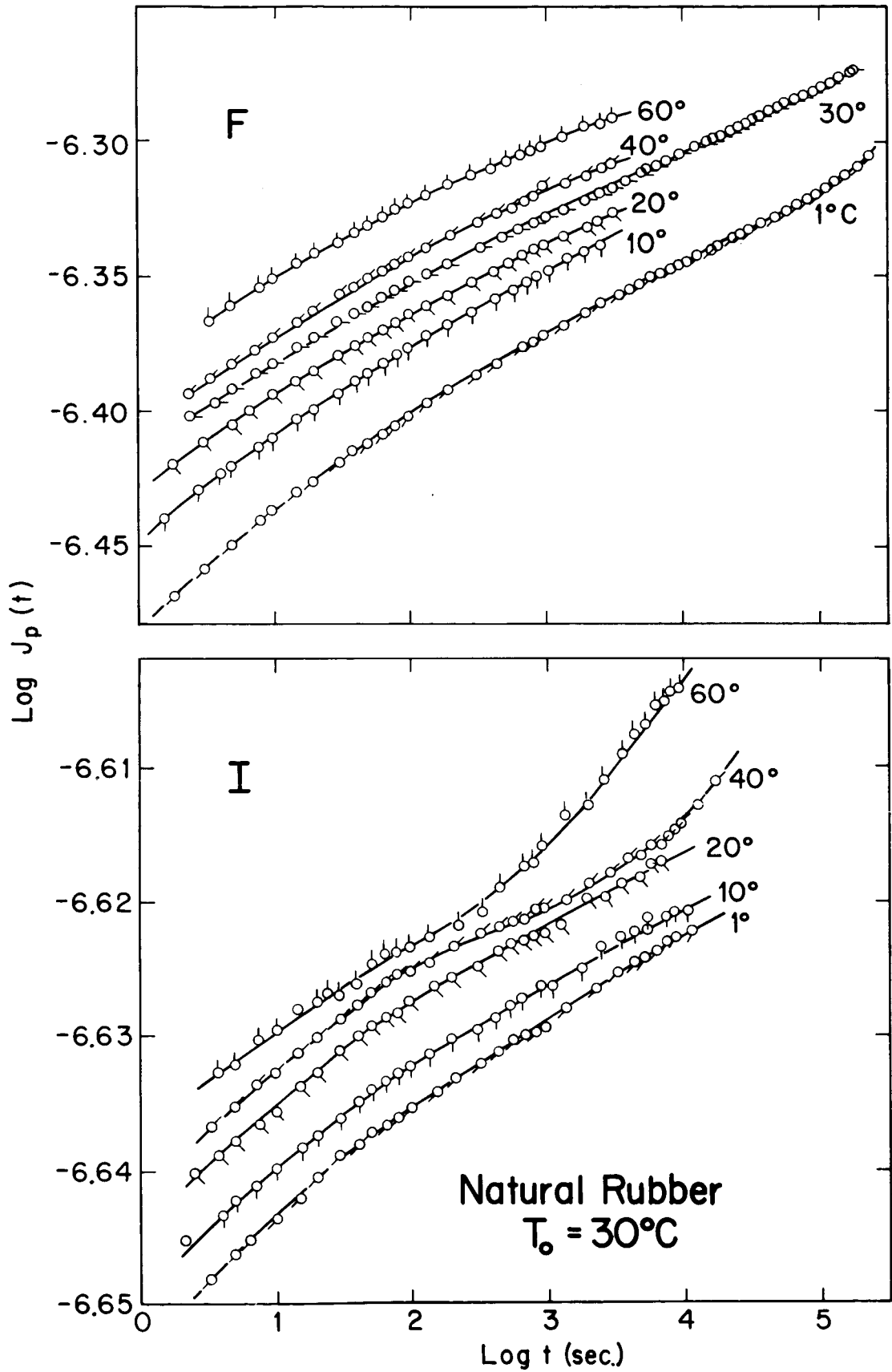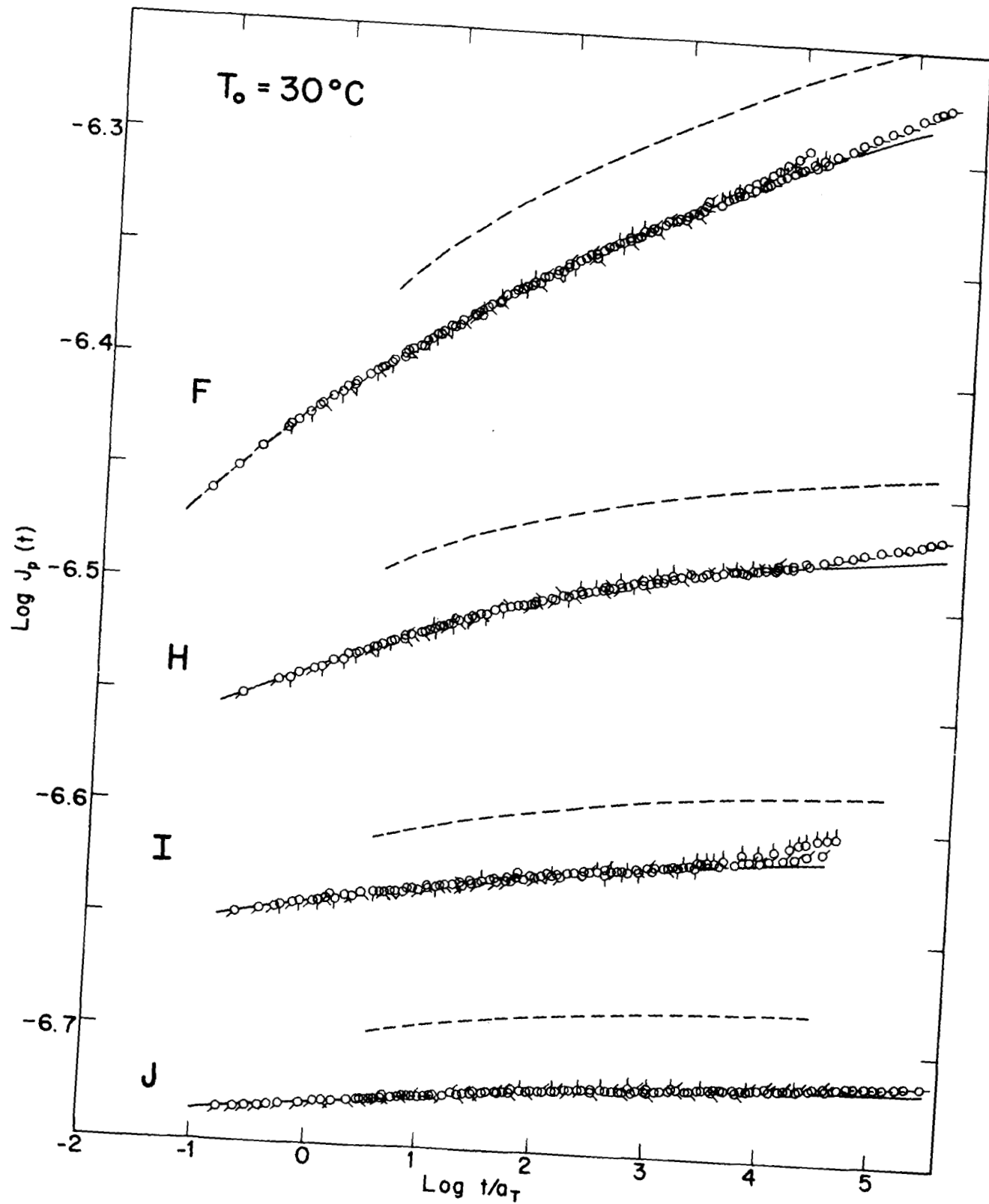Dashed line from Fig. 4. Dotted lines indicate a decomposition
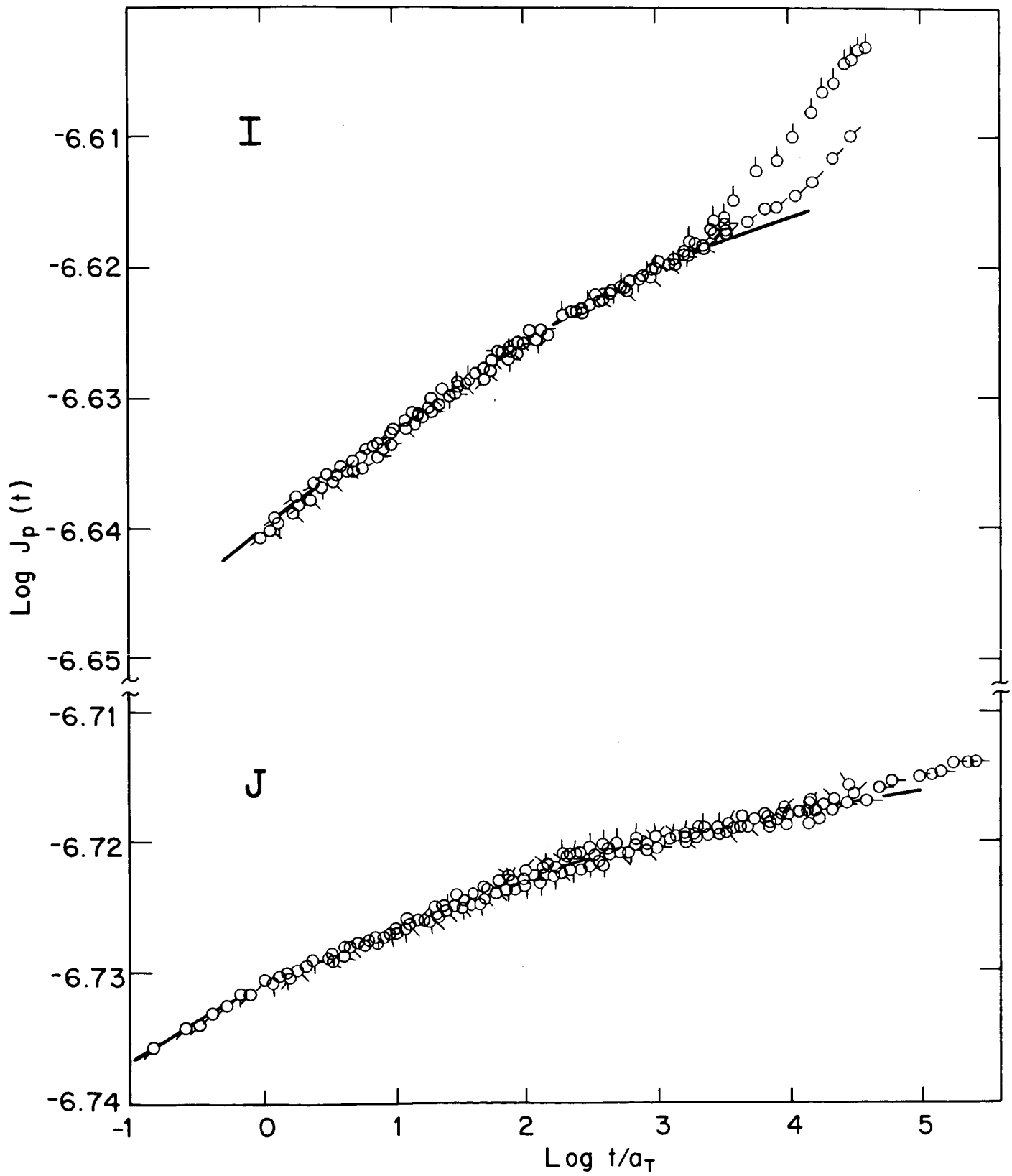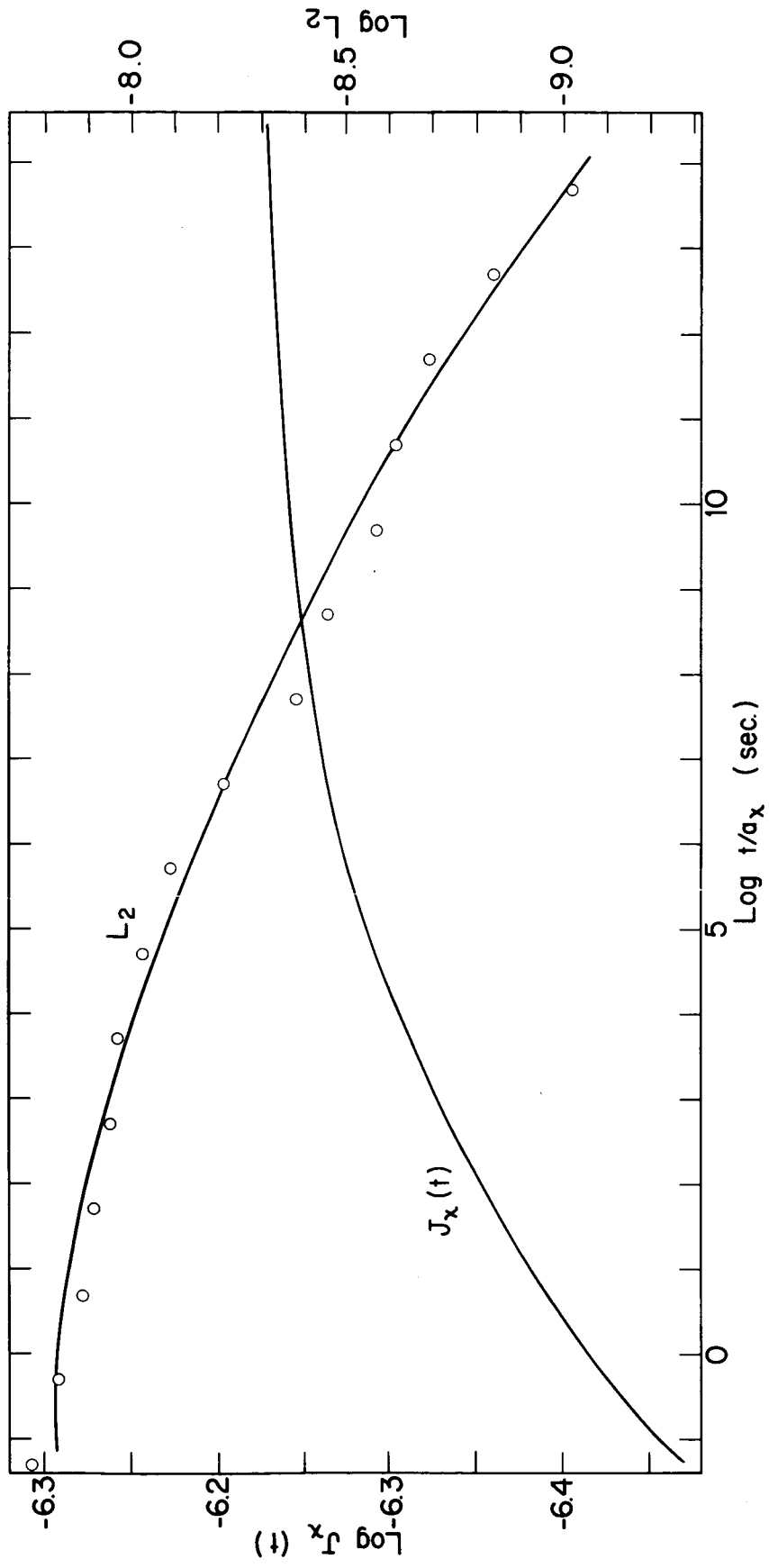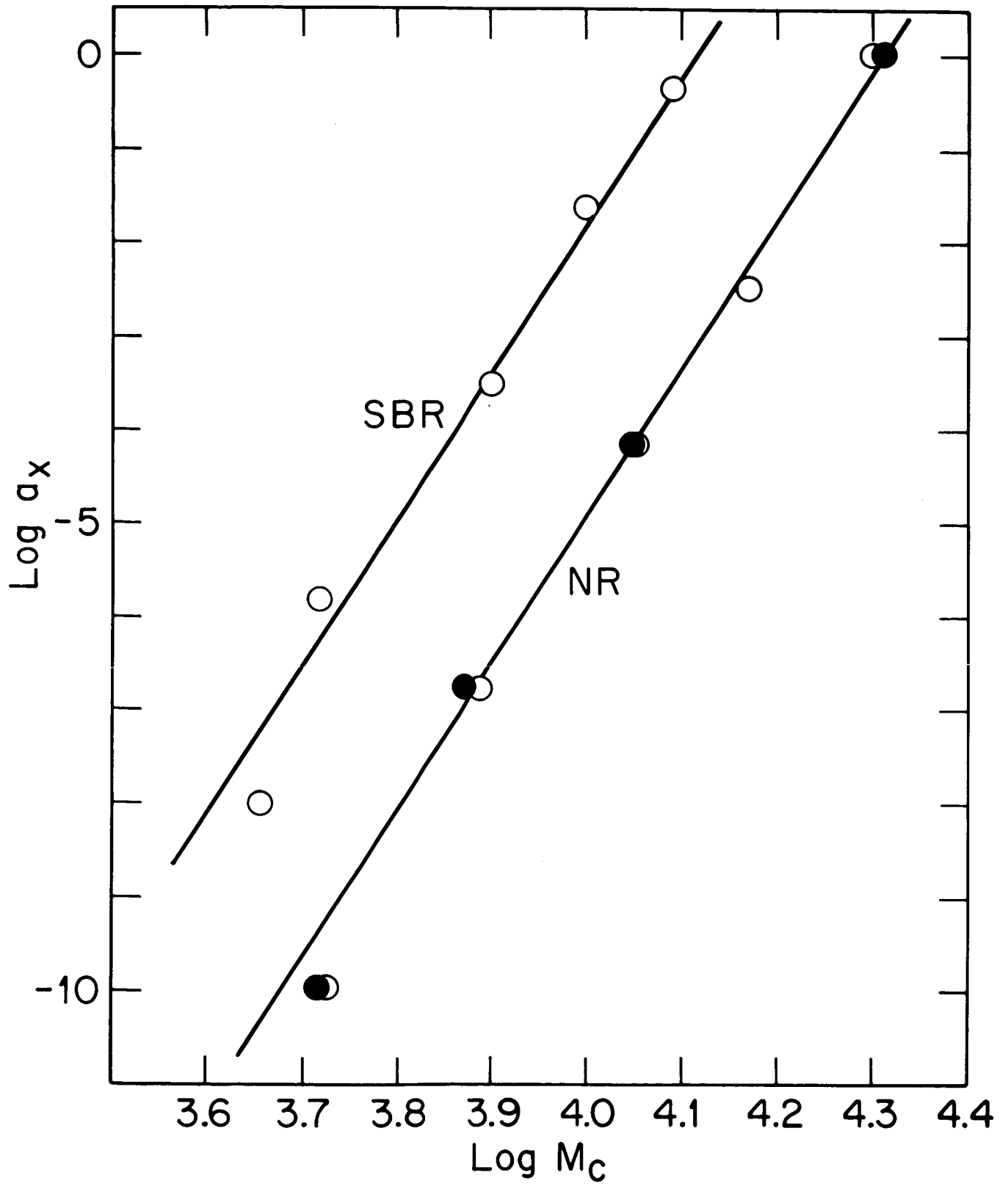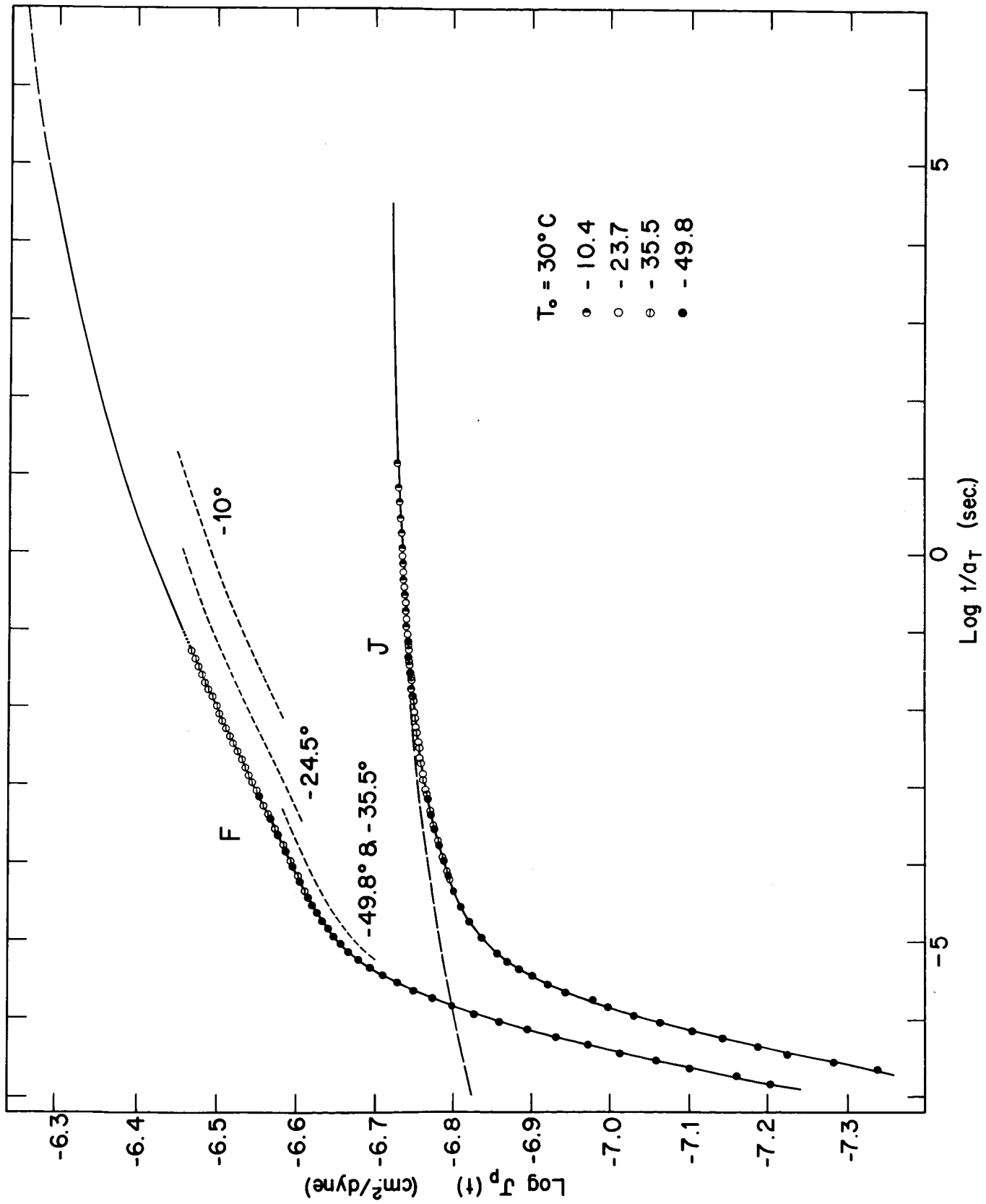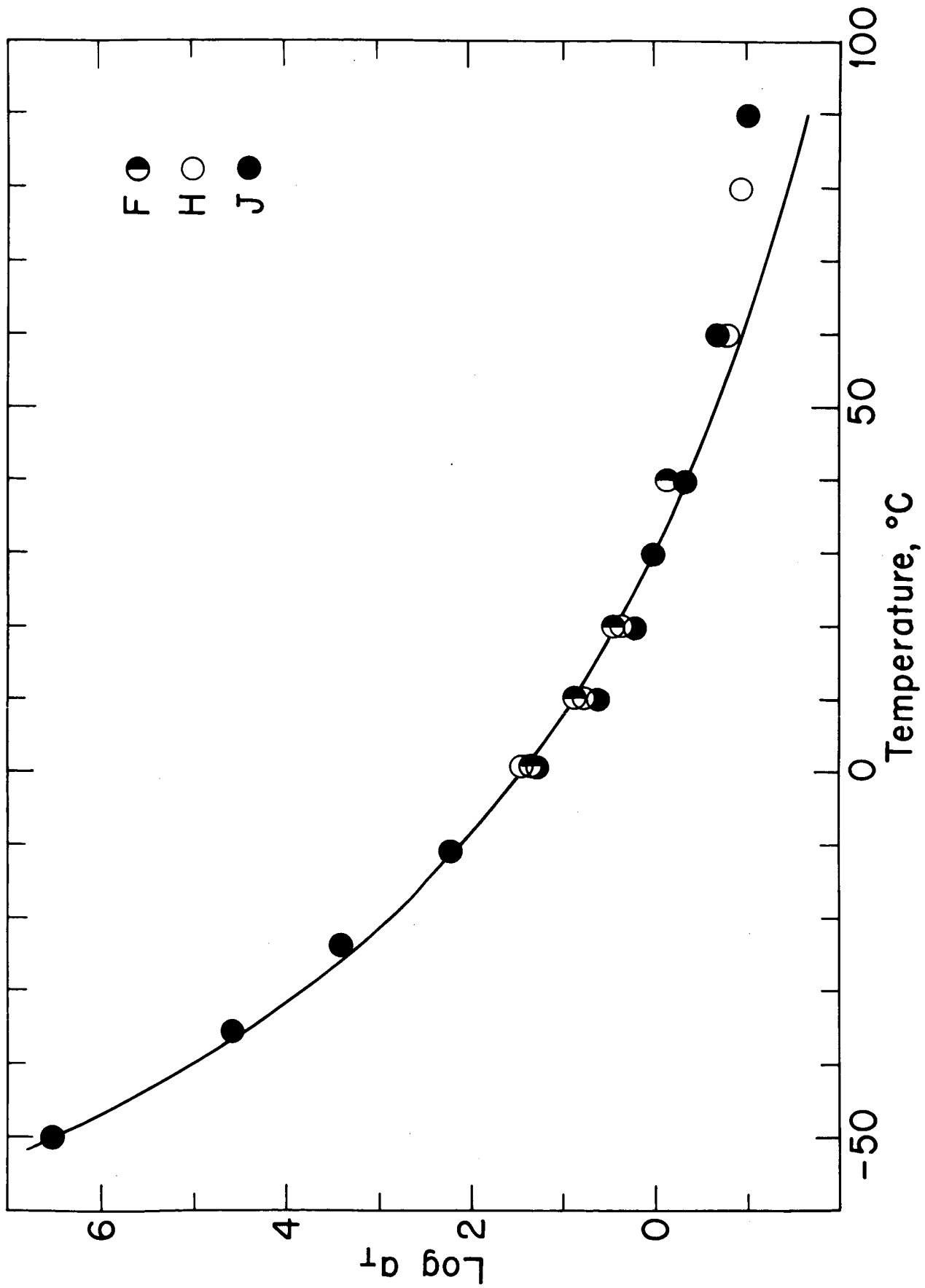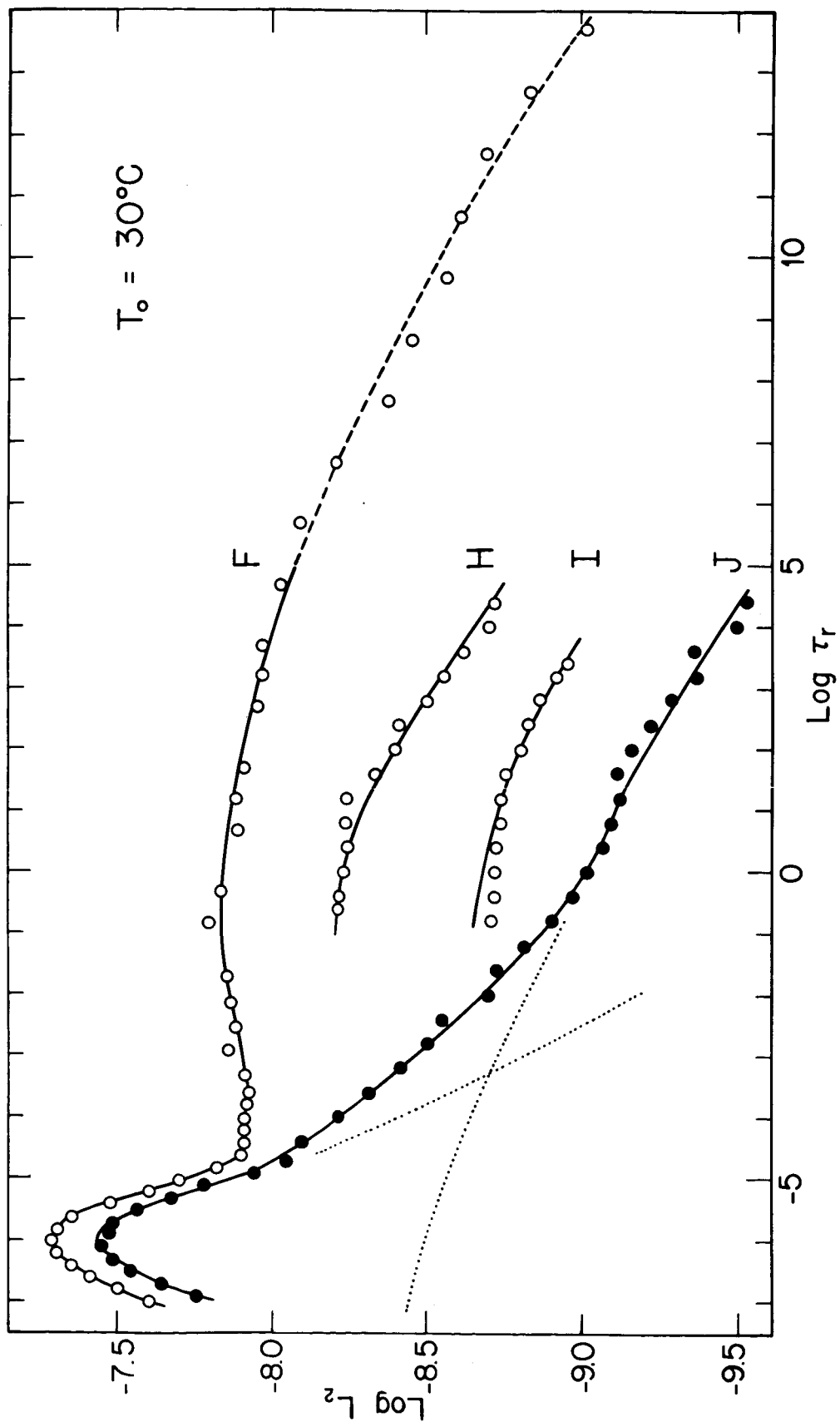of the spectrum of J.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8