

OFFICE OF NAVAL RESEARCH

2

GRANT OR CONTRACT N00014-88-K-0302

AD-A237 430



R&T Code 413m 010

Technical Report No. 7

DTIC ELECTE JUN 21 1991 C D

Model Filled Polymers VII: Flow Behavior of Polymers Containing Monodisperse Crosslinked Polymeric Beads

by

Liqing Sun, Moonsoo Park, J. J. Aklonis* and R. Salovey

Prepared for Publication

in

Polymer Engineering and Science

University of Southern California
Department of Chemical Engineering
*Department of Chemistry
Los Angeles, California 90089-1211

May 10, 1991

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sales; its distribution is unlimited.

This statement should also appear in Item 10 of the Document Control Data-DD Form 1473. Copies of the form available from cognizant grant or contract administrator.

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/ _____	
Availability Codes	
Dist	Avail and/or Special
A-1	



91-02946



REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified		1b RESTRICTIVE MARKINGS	
2a SECURITY CLASSIFICATION AUTHORITY		3 DISTRIBUTION/AVAILABILITY OF REPORT Unlimited	
2b DECLASSIFICATION/DOWNGRADING SCHEDULE		5 MONITORING ORGANIZATION REPORT NUMBER(S)	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 7		7a NAME OF MONITORING ORGANIZATION Office of Naval Research	
6a NAME OF PERFORMING ORGANIZATION University of Southern California	6b OFFICE SYMBOL (if applicable) MC 1211	7b ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, Virginia 22217-5000	
6c ADDRESS (City, State, and ZIP Code) Department of Chemical Engineering University of Southern California Los Angeles, California 90089-1211		9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER ONR N00014-88-K-0302	
8a NAME OF FUNDING/SPONSORING ORGANIZATION ONR/DARPA	8b OFFICE SYMBOL (if applicable)	10 SOURCE OF FUNDING NUMBERS	
1c ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, Virginia 22217-5000		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
1 TITLE (Include Security Classification) Model Filled Polymers VII: Flow Behavior of Polymers Containing Monodisperse Crosslinked Polymeric Beads			
2 PERSONAL AUTHOR(S) Liqing Sun, Moonsoo Park, J. J. Aklonis and R. Salovey			
3a TYPE OF REPORT Technical	13b TIME COVERED FROM 9/1/90 TO 5/1/91	14 DATE OF REPORT (Year, Month, Day) 1991, May 10	15 PAGE COUNT 36
6. SUPPLEMENTARY NOTATION Submitted to <u>Polymer Engineering and Science</u>			
7 COSAH CODES		18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		Filled Polymers; Crosslinked Monodisperse Polymeric Beads; Rheology	
9. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>Steady shear viscosities and dynamic moduli of polymer composites, consisting of combinations of crosslinked beads and matrices of polystyrene (PS) and polymethacrylates (PMA), are measured in a cone and plate rheometer. Viscosities and moduli were very sensitive to chemical composition. Crosslinked beads of identical composition to the matrix exhibited the lowest viscosity enhancements at low shear rates and the lowest moduli in dynamic mechanical analysis. The effects of bead concentration on rheological behavior were compared for PS and PMMA beads in a PMMA matrix. PMMA beads produce small effects, whereas, PS beads yielded highly non-Newtonian systems in PMMA, showing a yield stress of 1100 Pa at 30 wt% filler loading, and dynamic moduli independent of frequency. We suggest that rheological behavior reflects the state of dispersion of beads in the matrix. Beads identical in composition to the matrix yield uniform dispersions. We propose that uniform and stable bead dispersions exhibit the lowest viscosity and moduli. Beads that cluster in the matrix, such as PS beads in PMMA, exhibit highly non-Newtonian behavior.</p>			
3 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21 ABSTRACT SECURITY CLASSIFICATION Unclassified	
8 NAME OF RESPONSIBLE INDIVIDUAL Dr. JoAnn Hillborn		22b TELEPHONE (Include Area Code) (703) 696-4407	22c OFFICE SYMBOL ONR

Model Filled Polymers VII: Flow Behavior of Polymers Containing Monodisperse Crosslinked Polymeric Beads^Δ

LIQING SUN, MOONSOO PARK, J. J. AKLONIS* and R. SALOVEY[†]

*Department of Chemical Engineering and *Department of Chemistry,
University of Southern California, Los Angeles, California 90089-1211*

[†]To whom all correspondence should be addressed.

^ΔPresented in part at ANTEC '91 in Montreal, May 8, 1991.

Model Filled Polymers VII: Flow Behavior of Polymers Containing Monodisperse Crosslinked Polymeric Beads

LIQING SUN, MOONSOO PARK, J. J. AKLONIS* and R. SALOVEY†

*Department of Chemical Engineering and *Department of Chemistry,*

University of Southern California, Los Angeles, California 90089-1211

ABSTRACT

Steady shear viscosities and dynamic moduli of polymer composites, consisting of combinations of crosslinked beads and matrices of polystyrene (PS) and polymethacrylates (PMA), are measured in a cone and plate rheometer. Viscosities and moduli were very sensitive to chemical composition. Crosslinked beads of identical composition to the matrix exhibited the lowest viscosity enhancements at low shear rates and the lowest moduli in dynamic mechanical analysis. The effects of bead concentration on rheological behavior were compared for PS and PMMA beads in a PMMA matrix. PMMA beads produce small effects, whereas, PS beads yielded highly non-Newtonian systems in PMMA, showing a yield stress of 1100 Pa at 30 wt% filler loading, and dynamic moduli independent of frequency. We suggest that rheological behavior reflects the state of dispersion of beads in the matrix. Beads identical in composition to the matrix yield uniform dispersions. We propose that uniform and stable bead dispersions exhibit the lowest viscosity and moduli. Beads that cluster in the matrix, such as PS beads in PMMA, exhibit highly non-Newtonian behavior.

†To whom all correspondence should be addressed.

Model Filled Polymers VII: Flow Behavior of Polymers Containing Monodisperse Crosslinked Polymeric Beads

LIQING SUN, MOONSOO PARK, J. J. AKLONIS* and R. SALOVEY†

*Department of Chemical Engineering and *Department of Chemistry,
University of Southern California, Los Angeles, California 90089-1211*

INTRODUCTION

Particulate fillers are often used to enhance the physical properties of polymers for the preparation of commercial plastics and rubbers. However, the incorporation of fillers alters the flow behavior or rheology of filled polymers, imposing constraints on material processing. A basic understanding of the rheology of filled polymers is of great scientific interest and has important practical implications [1-4].

Ordinarily, the addition of fillers increases the steady shear viscosity of polymer melts. At low concentrations of filler, many polymers preserve a Newtonian plateau in viscosity, exhibited at low shear rates. However, at high filler loadings, the viscosity may become non-Newtonian at all shear rates and unbounded at low shear stress, showing a yield phenomenon. We have reported on the rheology of model polymer composites consisting of polystyrene filled with monodisperse crosslinked polystyrene beads [5].

The importance of filler/matrix interactions has been demonstrated by examining the effects of coupling agents and surface treatments on the rheological behavior of filled systems. Coupling agents are believed to concentrate at the interface between filler and matrix and increase the adhesion. Coupling agents have been used to reduce the melt viscosity of filled polypropylene [6-9]. For example, a titanate coupling agent enhanced the compatibility of inorganic fillers with

†To whom all correspondence should be addressed.

polypropylene, perhaps, improving the dispersion of isolated filler particles, and reducing the melt viscosity [8]. However, the addition of specific coupling agents could change the melt viscosity of polymer composites containing glass beads, in either direction, or not at all [7, 9]. Apparently, coupling agents do not, necessarily, improve the dispersion of filler particles.

Similarly, the surface treatment of inorganic fillers effects rheological changes. Surface treatment of CaCO_3 filler produced reductions in both viscosity and yield stress in filled polystyrene [8, 10]. It was inferred that a surface coating reduced the interaction between filler particles and, so, reduced particle aggregation [10]. An aggregation of filler particles leads to increases in melt viscosity, yield stress and dynamic moduli [11-15]. The dynamic moduli of polymer composites were affected by the surface treatment of fillers [16, 17]. In fact, the surface treatment of 15 μm stainless steel spheres affected the rheology of polyethylene composites [18]. A reduction of viscosity occurs if surface treatment acts to wet and disperse the filler. An increase in viscosity will occur if surface treatment increases the adhesion between filler and polymer. Both processes can occur simultaneously, if the filler particles are submicron and have a tendency to form loose agglomerates. A decreased aggregation of silica, in suspensions in low molecular weight analogs of elastomers [19], results from modification of the surface of silica by grafting. Newtonian or yield behavior could be controllably produced in coal slurries, by varying particle interactions by changing the surface charge density or the ionic strength of the medium [20]. A yield phenomenon was observed when coal particles do not repel, while a minimum viscosity results when the suspension is close to a transition from attractive to repulsive particle interaction [20].

Changes in the nature and molecular weight of the polymer matrix, also, affect the rheology of composites. The effects of filler are enhanced by reducing the matrix viscosity [21] and the pseudoplastic flow of suspensions increased with decreasing matrix viscosity [22]. A model of interparticle interaction, via entanglement of polymer molecules adsorbed on the filler surface, has been proposed [23]. Matrix polarity strongly affects the non-Newtonian behavior of

interacting particles [24]. Graphite suspensions are substantially more pseudoplastic, and exhibit a higher power law index, than polystyrene bead suspensions. The pseudoplasticity, or sensitivity to shear rate, of graphite suspensions increases with decreasing liquid polarity. This behavior was attributed to increased interparticle van der Waals interaction with reduced medium polarity.

The rheological behavior of suspensions of crosslinked polymeric beads in polymer solutions or low molecular weight liquids has been reported [25-30]. The steady flow and dynamic viscoelastic properties of dispersions of crosslinked polystyrene beads of various sizes in polystyrene solutions were studied [25]. A yield stress was observed to increase with increasing bead content, decreasing bead size and increasing polystyrene concentration in solution, factors that enhance bead-bead interaction and agglomeration. The viscoelastic behavior of concentrated suspensions of grafted polymethyl methacrylate (PMMA) beads was examined [26]. A sharp transition in dynamic viscosity is shown over a narrow frequency range. It was suggested that a reduction in bead packing density occurred, allowing dynamic shear flow. Similar studies of PMMA beads dispersed in silicone fluids demonstrated distinct types of rheological behavior depending on matrix molecular weight [27]. A recent study reports on the rheology of dispersions of crosslinked polystyrene beads in polystyrene solutions [28]. A yield stress observed in creep experiments is of a magnitude calculated for a bead superstructure. In steady shear flow at higher shear rates, the viscosity approaches a Newtonian plateau as the agglomerated bead structure is decomposed. The rate of shear-induced flocculation of polystyrene spheres in hydroxyethyl cellulose solutions was affected by the viscoelasticity of the suspending medium [29]. At shear rates at which elasticity dominates relative to viscous forces, flocculation rates were found to be at least an order of magnitude less than those expected for suspensions in a Newtonian fluid. The rheology of suspensions of monodisperse PMMA particles with a chemically attached stabilizer layer has been reported [30]. The ratio between the particle radius and stabilizer layer thickness was changed between 5 and 61. At high values of this ratio, Brownian hard sphere behavior is exhibited. At lower values, deviations in rheological behavior are assigned to a soft stabilizer layer.

In order to elucidate the interactions of polymeric fillers and matrices, we have extended research on bead filled polymers [5, 31] to include polymethacrylate beads and matrices. In this paper, we report on the effects of incorporating polymeric beads of different compositions, in a series of polymeric matrices, on the steady shear viscosity and dynamic moduli.

EXPERIMENTAL DETAILS

Materials

Polystyrene (PS) was obtained from Dow Chemical Co. and has an average molecular weight (\bar{M}_w) of 250,000, ascertained by gel permeation chromatography (GPC, Waters) calibrated with monodisperse polystyrene standards. Polymethyl methacrylate (PMMA) was purchased from Scientific Polymer Products, Inc. and has $\bar{M}_w = 36,000$, as determined by GPC with PMMA standards. Polybutyl methacrylate (PBMA) was also purchased from Scientific Polymer Products and gives $\bar{M}_w = 170,000$ by GPC, with PMMA standards. These polymers were used as matrices in the preparation of filled composites.

Crosslinked monodisperse polymer beads of controlled size ($0.4 \pm 0.05 \mu\text{m}$ diameter by scanning electron microscopy) synthesized in emulsifier-free emulsion polymerization [31, 32], were used as filler particles. Beads were crosslinked by copolymerization with 2 mole% divinyl benzene (DVB) for the PS beads or 2 mole% ethylene glycol dimethacrylate (EGDMA) for the polymethacrylate beads.

Sample Preparation

Powdered filler particles are added to a molten (matrix) polymer containing antioxidant [33] in the mixing chamber of a Brabender Plasticorder and mixed at elevated temperatures, up to 175°C , for 15 minutes at equal time intervals of 50 and 100 rpm. Mixed samples are placed inside a flat concentric circular mold and compression molded at 175°C and $1.5 \times 10^7 \text{ Pa}$ in a Duke

Hydraulic Press for 15 minutes and then cooled to room temperature.

Rheology

Steady shear viscosity and first normal stress difference of molten composites are measured at 200°C for PS and PMMA composites or at 150°C for PBMA composites with a Weissenberg Rheogoniometer, in a cone and plate geometry. The bottom platen is a cone of 5 cm diameter and 0.034 radian (2°) cone angle. The top platen is a 5 cm diameter flat disk. The maximum range of shear rates varies from 1.4×10^{-3} to 14 sec^{-1} . We have also recorded the stress output as a function of time. The instrument compliance is calculated to be very small. Storage and loss moduli were also measured for the same systems at 150 and 200°C. For dynamic mechanical analysis, the cone is subjected to forced sinusoidal oscillations. The strain amplitude is 5%. The sinusoidal shear generated by the oscillating cone transmits a torque via the sample to the top platen, which is constrained by a torsion bar, and oscillates with different amplitude and phase. The range of frequencies used is 2×10^{-3} to 20 Hz.

RESULTS

The steady shear viscosity as a function of shear rate of polystyrene (PS), filled with 20% of crosslinked polymeric beads, is illustrated in Figure 1. Storage and loss moduli at various frequencies for these systems are shown in Figures 2 and 3, respectively. If a lower molecular weight PS matrix ($\bar{M}_w = 76,000$) is used for these composites, both steady shear viscosity and dynamic moduli of filled systems are enhanced much more, in comparison to pure PS, by the inclusion of polymeric beads, than the system illustrated. However, while beads of different composition showed the same trends as those illustrated, low molecular weight PS composites, filled with beads of different compositions, are not as easily distinguishable, rheologically. In all cases with the PS matrix, polybutyl methacrylate (PBMA) beads produced the largest increases in steady shear viscosity at low shear rates and in dynamic moduli. With the lower molecular weight PS matrix, PS and polymethylmethacrylate (PMMA) beads of varied crosslink densities, from 2

10 mol%, show little difference in steady shear viscosity and dynamic moduli.

The steady shear viscosity of PMMA matrix filled with 20% of crosslinked polymeric beads is illustrated in Figure 4. From measurements of stress output as a function of time in steady shear experiments, we find that the total strain approximates 7, when the stress output of the composite reaches a steady state, depending on the nature of the composite and the shear rate. At low shear rates, stress curves are smooth and show initial monotonic increases with time. At higher shear rates, we observe stress overshoot, associated with the yield phenomena. A comparison of the stress output from steady shear experiments on composites of 20% PS beads or 20% PMMA beads in the PMMA matrix, indicates that the latter system stabilizes readily (between 10-30 seconds), while the former stabilizes slowly and exhibits stress overshoot at higher shear rates. Storage and loss moduli for composites with a PMMA matrix are shown in Figures 5 and 6, respectively. In the PMMA matrix, PS beads of different crosslink densities, from 2-10 mol%, produce little difference in steady shear viscosity and dynamic moduli.

The steady shear viscosity of PBMA matrix filled with 20% of crosslinked polymeric beads is shown in Figure 7. Storage and loss moduli for the PBMA system are shown in Figures 8 and 9, respectively. Again, in the PBMA matrix, PS beads of varied crosslink densities, from 2-10 mol%, produce similar rheological behavior.

The steady shear viscosity of PMMA matrix filled with various concentrations of crosslinked (2 mol%) PS beads, up to 40 weight%, is shown in Figure 10. Corresponding dynamic moduli are shown in Figures 11 and 12. The steady shear viscosity of the PMMA matrix containing up to 40 weight% crosslinked (2 mol%) PMMA beads is shown in Figure 13. Corresponding dynamic moduli are plotted in Figures 14 and 15.

DISCUSSION

We have previously reported that polymer composites, containing monodisperse sized

crosslinked PS beads in a PS matrix, exhibit rheological behavior, in steady or oscillatory shear, essentially, independent of bead size, from 200-800 nm, and crosslink density, from 1-10 mol% crosslinks [5]. Similarly, in these studies, PS beads varying in crosslink density from 2-10 mol%, do not differ in steady shear viscosity or dynamic moduli in several polymer matrices, including PMMA, PBMA or a lower molecular weight PS. Moreover, PMMA beads of crosslink density, varying from 2-10 mol%, do not differ rheologically in the low molecular weight PS matrix. Current results are consistent with our earlier conclusion of an increase in steady shear viscosity and dynamic moduli of polymer composites, with increasing volume fraction of crosslinked polymeric beads, independent of bead size and crosslink density. However, we observe that rheological behavior is particularly sensitive to the *composition* of polymeric beads and matrices.

With increasing volume fraction of beads, filled composites often approach yield behavior, in which the shear stress becomes independent of shear rate, calculated viscosities become unbounded and low frequency dynamic moduli become independent of frequency. Yield behavior results when filled melts exhibit solid-like behavior. It has been suggested [12-15], that the yield phenomenon corresponds to the formation of an independent network of filler particles that precludes flow. The formation of such a network depends on the interactions between beads, and between beads and matrix, which affect the dispersion of beads, leading to bead agglomeration. These interactions are, apparently, not sensitive to bead size (within a narrow range), nor to bead crosslink density. However, such interactions are sensitive to the composition of beads and matrix.

Studies of the onset of yield behavior can be readily made by examining the slopes of double log plots of steady shear viscosity against shear rate, as well as, slopes of double log plots of dynamic moduli versus frequency. Moreover, plots of shear stress versus strain rate, can be analyzed to derive the magnitude of yield stresses. In steady shear rheology of polymer composites achieving yield behavior, the slope of the steady shear viscosity, on a double logarithmic plot against shear rate, approaches -1. Since the viscosity is calculated from the ratio of shear stress to shear (strain) rate, a slope of -1 indicates an independence of shear stress and shear rate. For the

system of polymeric beads in a PS matrix (Figure 1), the composite becomes more non-Newtonian than the pure matrix, upon the addition of polymeric beads. Pure PS shows a Newtonian plateau at low shear rates, as the steady shear viscosity is (almost) independent of shear rate. This would be true for a larger range of shear rates, if the PS were of lower molar mass [12]. Here, since the pure PS matrix is of relatively high molar mass, the steady shear viscosity of PS exhibits non-Newtonian behavior at increased shear rate [5]. At the higher shear rates, the viscosity decreases (almost) linearly with shear rate (on the double log plot), signifying shear thinning and power-law behavior. Shear thinning, ordinarily, increases with the addition of polymeric beads [5]. The lowest effect, among the various polymeric beads, is noted for crosslinked PS beads, which are "compatible" with the PS matrix, leading to a uniform dispersion of PS beads in the PS matrix. The slopes of the steady shear viscosity at low shear rates increase *absolutely* from -0.07 to -0.37 as we proceed from PS to PMMA to PEMA to PBMA beads. Corresponding, calculated solubility parameter values are 9.5 (PS), 9.0 (PMMA), 8.9 (PEMA) and 8.7 (PBMA) [34]. Solubility parameters measure the interactions between molecules, and show that the PS matrix varies its miscibility with polymeric beads of different composition. As a result, PBMA beads are more likely to approach yield behavior, by agglomerating within the PS matrix, and PS filled with PBMA beads showed the largest negative slope. Yield stresses for the polymeric composites may be estimated from Casson plots of the square root of shear stress against the square root of shear rate [25, 35, 36]. While, none of the PS composites clearly exhibits yield behavior, an apparent yield stress may be derived, which increases for 20% filled PS composites, in the order PS < PMMA < PEMA < PBMA, reaching 146 Pa for the latter system. This value is similar to the yield stress for 30% of low surface area carbon black dispersed in a PS matrix [13].

Corresponding plots of dynamic moduli (Figures 2 and 3) indicate initial slopes of 1.25 for G' and 0.95 for G'' for pure PS. Since the strain amplitude in our oscillatory measurements approximates 5%, we believe that the dynamic mechanical data are in a linear range. Linear viscoelastic liquids would exhibit corresponding slopes of 2 and 1, respectively [37]. The slope of the storage modulus, G' , decreases from 2, depending on the molecular weight of the PS matrix.

system of polymeric beads in a PS matrix (Figure 1), the composite becomes more non-Newtonian, than the pure matrix, upon the addition of polymeric beads. Pure PS shows a Newtonian plateau at low shear rates, as the steady shear viscosity is (almost) independent of shear rate. This would be true for a larger range of shear rates, if the PS were of lower molar mass [12]. Here, since the pure PS matrix is of relatively high molar mass, the steady shear viscosity of PS exhibits non-Newtonian behavior at increased shear rate [5]. At the higher shear rates, the viscosity decreases (almost) linearly with shear rate (on the double log plot), signifying shear thinning and power law behavior. Shear thinning, ordinarily, increases with the addition of polymeric beads [5]. The lowest effect, among the various polymeric beads, is noted for crosslinked PS beads, which are "compatible" with the PS matrix, leading to a uniform dispersion of PS beads in the PS matrix. The slopes of the steady shear viscosity at low shear rates increase *absolutely* from -0.07 to -0.37, as we proceed from PS to PMMA to PEMA to PBMA beads. Corresponding, calculated solubility parameter values are 9.5 (PS), 9.0 (PMMA), 8.9 (PEMA) and 8.7 (PBMA) [34]. Solubility parameters measure the interactions between molecules, and show that the PS matrix varies in miscibility with polymeric beads of different composition. As a result, PBMA beads are most likely to approach yield behavior, by agglomerating within the PS matrix, and PS filled with PBMA beads showed the largest negative slope. Yield stresses for the polymeric composites may be estimated from Casson plots of the square root of shear stress against the square root of shear rate [25, 35, 36]. While, none of the PS composites clearly exhibits yield behavior, an apparent yield stress may be derived, which increases for 20% filled PS composites, in the order PS < PMMA < PEMA < PBMA, reaching 146 Pa for the latter system. This value is similar to the yield stress for 30% of low surface area carbon black dispersed in a PS matrix [13].

Corresponding plots of dynamic moduli (Figures 2 and 3) indicate initial slopes of 1.25 for G' and 0.95 for G'' for pure PS. Since the strain amplitude in our oscillatory measurements approximates 5%, we believe that the dynamic mechanical data are in a linear range. Linear viscoelastic liquids would exhibit corresponding slopes of 2 and 1, respectively [37]. The slope of the storage modulus, G' , decreases from 2, depending on the molecular weight of the PS matrix.

Comparison of initial slopes of $\log G'$ versus $\log \omega$ at 200°C have been reported [5]. The slope of the loss modulus curve is much less sensitive to molar mass. With the addition of filler, slopes of dynamic moduli decrease as filled composites deviate further from Newtonian behavior. Again, the initial slope of G' decreases, in the same order of bead composition observed for "increasing" steady shear viscosity, to 0.70 for PBMA beads (Figure 2), while the initial slope of G'' has decreased to 0.72 for PBMA beads (Figure 3). A comparison of dynamic mechanical and steady shear data indicates that the Cox-Merz relation [38-43] is not applicable to filled polymers.

Similarly, we can compare beads of different composition in a PMMA matrix. The steady shear viscosity of pure PMMA is slightly shear thinning over the range of shear rates measured (Figure 4). The zero shear viscosity of pure PMMA approximates 2300 Pa.s, which is more than two orders of magnitude higher than PS of comparable molar mass [12]. The viscosity of polymer melts depends on the number of atoms in the chain backbone (proportional to molar mass) and a temperature dependent friction factor per chain atom [44]. A marked change in the molar mass dependence occurs above the entanglement molecular weight of the polymer. Since, the entanglement molecular weight for PMMA is lower than that of PS [45], the melt viscosity of a larger fraction of PMMA molecules varies approximately as $M^{3.4}$, whereas, many PS molecules vary linearly with molar mass [45]. Moreover, the friction factor for PMMA is much higher than that for PS [46]. The addition of 20% PMMA beads leads to a very large increase in viscosity, producing an almost parallel curve to that for the pure matrix (Figure 4). Large viscosity enhancements and parallel curves have been reported for dispersions of carbon black in a PBMA matrix [12]. It was suggested, that increased interactions, between a polar filler and a polar matrix, lead to large increases in steady shear viscosity. Similarly, increasing polar interactions in the PBMA matrix (Figure 7) lead to large enhancements in steady shear viscosity. In the PMMA matrix, PS beads exhibit an initial slope of steady shear viscosity of -0.7, PEMA beads show a slope of -0.49 and PBMA beads show a slope of -0.56 (Figure 4). Thus, PS beads appear to be least compatible with the PMMA matrix and composites approach yield behavior. The difference in

solubility parameter, $\Delta\delta$, is the largest for PS beads in a PMMA matrix. Dynamic moduli show analogous results. In the PMMA matrix, PS and PBMA beads produce the largest effects and approach yield behavior, with the initial slope of G' approximating 0.21 (Figure 5), while G'' approximates 0.34 (Figure 6), for composites of the PMMA matrix containing either PS or PBMA beads. Dynamic moduli of pure PMMA are not linear with frequency on double logarithmic plots (Figures 5 and 6), probably as a result of high polar interactions between PMMA molecules. With increasing hydrocarbon content, both PS and PBMA beads are less miscible with the PMMA matrix, and show $\Delta\delta \sim 0.3-0.5$, and tend to agglomerate and approach yield behavior. PEMA beads exhibit intermediate behavior. Calculations of apparent yield stresses from Casson plots [25, 35, 36], for the PMMA matrix, show that the highest yield stress corresponds to PS beads (429 Pa), PBMA beads are next (345 Pa), then, PEMA beads (115 Pa), while PMMA beads do not induce a yield stress with a PMMA matrix.

The steady shear viscosity of pure PBMA at 150°C is very similar in magnitude and shear rate dependence to that of pure PMMA at 200°C. The zero shear viscosity of PMMA is 2300 Pa (Figure 4) while that of PBMA is 2000 Pa (Figure 7). The weight average molar mass (\bar{M}_w) of the PBMA is determined by GPC to be 170,000, using a PMMA calibration, while \bar{M}_w of the PMMA is 36,000 from GPC using a PMMA calibration. Thus, \bar{M}_w for PBMA is almost 5 times that of PMMA. Again, the entanglement spacing for PBMA considerably exceeds that for PMMA [45], so that, for PMMA, the steady shear viscosity would be a higher function of \bar{M}_w .

The steady shear viscosity of filled PBMA composites produces a series of parallel lines with small power law slopes (-0.27), (Figure 7). However, the minimum viscosity enhancement is shown by the inclusion of PBMA beads in the PBMA matrix. Again, beads of identical composition to the matrix, are most likely to be uniformly dispersed and least likely to agglomerate. Apparently, *uniform* and *stable* bead dispersions exhibit the lowest rheological parameters. Similarly, dynamic moduli increase on the addition of crosslinked polymeric beads, with similar enhancements for PS and PMMA beads, and minimum enhancement for PBMA beads

(Figures 8 and 9).

Compared to beads of different composition, PBMA beads show, relatively, the smallest increases in steady shear viscosity and dynamic moduli in a PBMA matrix. The overall increase in steady shear viscosity and dynamic moduli, caused by the addition of PBMA beads to the PBMA matrix, is large, because of strong polar interactions between bead and matrix. Moreover, G' and G'' curves, for PBMA beads in the PBMA matrix, are "normally" shaped and approach linear (Newtonian) behavior at low frequencies, with slopes of 1.05 (Figure 8) and 0.84 (Figure 9), respectively. Casson plots [25, 35, 36] of shear stresses for PBMA composites exhibit a very low yield stress (73 Pa) for both PMMA and PS beads in PBMA matrix and only 46 Pa for PBMA beads in PBMA. Yield stresses calculated from steady shear data indicate the strength of a filler network or the agglomerates of beads that impede flow. The highest yield stresses were calculated for PS (429 Pa) and PBMA (345 Pa) beads in the PMMA matrix.

The development of a yield stress may be seen by increasing the concentration of beads in a matrix in which the beads are immiscible. Accordingly, we compared the effects of loading a PMMA matrix with various concentrations of PMMA and PS beads. Corresponding studies of PMMA and PS beads in a PS matrix showed that, in such composites, these beads were rheologically indistinguishable (Figures 1, 2 and 3). In the non-polar PS matrix, PMMA and PS beads appear to behave similarly. PS composites with increased $\Delta\delta$ [34], such as PEMA or PBMA beads, in a PS matrix, exhibit increased rheological enhancement. The steady shear viscosity of PMMA matrix, filled with various concentrations of crosslinked PS beads (Figure 10), shows yield behavior at 30 and 40% filler loading. For both these compositions, the slope of the steady shear viscosity versus shear rate is -1 on a double log plot at low shear rates. Similarly, for these concentrations of PS beads in the PMMA matrix, dynamic moduli became almost horizontal or independent of frequency at low frequencies (Figures 11 and 12). Because PS molecules at the bead surfaces are rejected by PMMA molecules in the matrix, PS beads may cluster in the PMMA matrix at elevated temperature. As a result, such composites exhibit highly non-Newtonian

behavior. Casson plots [25, 35, 36] extrapolate to yield stresses for 30% of PS beads of 1082 Pa and for 40% PS beads of 2362 Pa, in the PMMA matrix. Such yield stresses are about an order of magnitude lower than those shown by carbon black of surface area $625 \text{ m}^2/\text{g}$ in various polymeric matrices, which for 30% loading shows a yield stress of $1.6 \times 10^4 \text{ Pa}$ [13]. The surface area of the 400 nm PS beads is $14 \text{ m}^2/\text{g}$. The yield stress for PBMA containing 30% carbon black of surface area $24 \text{ m}^2/\text{g}$ is reported to be 430 Pa [13].

If we examine the PMMA matrix filled with various amounts of crosslinked PMMA beads, we find steady shear viscosities exhibiting slight power law dependence (Figure 13) and dynamic moduli with almost parallel curves (Figures 14 and 15). In the PMMA matrix, it is likely that PMMA beads are uniformly dispersed, and remain so, at moderate shear rates and frequencies. As a result, rheological enhancements are minimal. Only at 40% loading, are there deviations from parallel curves of storage modulus versus frequency (Figure 14). Casson plots [25, 35, 36] for PMMA beads in the PMMA matrix, fail to show a yield stress, even up to 40% loading.

CONCLUSIONS

Steady shear viscosities and dynamic moduli of polymer composites, consisting of combinations of polystyrene (PS) and polymethacrylates (PMA), increase with increasing volume fraction of crosslinked polymeric beads, independent of the crosslink density of the beads, from 2-10 mol% crosslinking. Viscosities and moduli were sensitive to the chemical composition of beads and matrices. In a PS matrix, PS and PMMA beads are, almost, rheologically indistinguishable. However, PBMA beads produce larger changes in a PS matrix. In a PMMA matrix, beads of different composition exhibit large differences in steady shear viscosity and dynamic moduli. Here, PS and PMMA beads differ widely, especially at low shear rates and frequencies. A large viscosity enhancement and a parallel curve of viscosity versus shear rate, compared to the pure PMMA matrix, characterize PMMA bead filled PMMA. Beads of other compositions produce highly non Newtonian composites with the PMMA matrix. PMMA composites, filled with PS or

PBMA beads, approach yield behavior, with PS bead filled PMMA showing the higher yield stress (429 Pa) at 20% loading. Bead filled PBMA composites produce curves of steady shear viscosities and dynamic moduli that are almost parallel to those of the pure PBMA matrix, and approach Newtonian behavior.

In general, crosslinked beads of identical chemical composition to the matrix exhibit the lowest viscosity enhancements in steady shear (at low shear rates) and the lowest moduli in dynamic mechanical analysis. We suggest that beads identical in composition to the matrix are most likely to be uniformly dispersed by mixing, during sample preparation, and least likely to agglomerate at elevated temperatures. Moreover, we propose that uniform and stable bead dispersions exhibit the lowest rheological parameters. This suggestion is supported by studies on PMMA matrices filled with various concentrations of PS and PMMA beads. For a PMMA matrix filled with up to 40 wt% PMMA beads, enhancements in steady shear viscosities or dynamic moduli are small and composites yield rheological curves that approach Newtonian behavior and are parallel to those for pure PMMA. In the PMMA matrix, it is likely that PMMA beads form uniform and stable dispersions. In sharp contrast, PS beads have very large rheological effects on the PMMA matrix. Large enhancements in steady shear viscosity result from the addition of PS beads and yield behavior is exhibited at 30 and 40% filler loading, as the shear stress becomes independent of shear rate, and yield stresses of 1100 and 2400 Pa are derived, respectively. Moreover, dynamic moduli for these systems become almost horizontal or independent of frequency at low frequencies. PS beads may coagulate in the PMMA matrix at elevated temperatures, forming networks of clustered beads. As a result, such composites exhibit highly non-Newtonian behavior. The shear stress becomes independent of shear rate and the dynamic moduli become independent of frequency. At higher shear rates, PS bead agglomerates are broken and the steady shear viscosities converge. Yield stresses may represent the strength of the bead network. These values were somewhat higher than corresponding yield stresses for carbon black of similar surface area.

ACKNOWLEDGEMENTS

This work was supported in part by the Office of Naval Research and by DARPA. We thank Dezhong Zou, Ruiling Guan and Shenmin Ma for assistance with sample preparation.

REFERENCES

1. A. B. Metzner, *J. Rheology*, **29**, 739 (1985).
2. M. R. Kamel and A. Mutel, *J. Polym. Eng.*, **5**, 293 (1985).
3. J. T. Byers and M. P. Wagner, in *Rubber Technology*, Chapter 3, 3rd Edition, edited by M. Morton, Van Nostrand Rheinhold, New York (1987).
4. Yu. G. Yanovsky and G. E. Zaikov, in *Polymer Yearbook*, **5**, edited by R. A. Pethrick, Harwood Academic Publishers, New York (1989), pages 61-86.
5. M. Park, K. Gandhi, L. Sun, J. J. Aklonis and R. Salovey, *Polym. Eng. and Sci.*, **30**, 1158 (1990).
6. M. S. Boaira and C. E. Chaffey, *Polym. Eng. and Sci.*, **17**, 715 (1977).
7. C. D. Han, C. Sandford and H. J. Yoo, *Polym. Eng. and Sci.*, **18**, 849 (1978).
8. H. Tanaka and J. L. White, *Polym. Eng. and Sci.*, **20**, 949 (1980).
9. C. D. Han, T. Van Den Weghe, P. Shte and J. R. Haw, *Polym. Eng. and Sci.*, **21**, 196 (1981).
10. Y. Suetsugu and J. L. White, *J. Appl. Polym. Sci.*, **28**, 1481 (1983).
11. K. Lakdawala and R. Salovey, *Polym. Eng. and Sci.*, **25**, 797 (1985).
12. K. Lakdawala and R. Salovey, *Polym. Eng. and Sci.*, **27**, 1035 (1987).
13. K. Lakdawala and R. Salovey, *Polym. Eng. and Sci.*, **27**, 1043 (1987).
14. K. Gandhi and R. Salovey, *Polym. Eng. and Sci.*, **28**, 877 (1988).
15. K. Gandhi and R. Salovey, *Polym. Eng. and Sci.*, **28**, 1628 (1988).
16. C. Scott, H. Ishida and F. H. J. Maurer, *Rheologica Acta*, **27**, 273 (1988).
17. J. D. Miller, H. Ishida and F. H. J. Maurer, *Rheologica Acta*, **27**, 397 (1988).
18. D. M. Bigg, *Polym. Eng. and Sci.*, **22**, 512 (1982).
19. W. M. Jiao, A. Vidal, E. Papirer and J. B. Donnet, *Colloids and Surfaces*, **40**, 279 (1989).
20. Y.-K. Leong and D. V. Boger, *J. Colloid and Interface Sci.*, **136**, 249 (1990).
21. N. Minagawa and J. L. White, *J. Appl. Polym. Sci.*, **20**, 501 (1976).
22. T. Ishihara, H. Katsuki and H. Kuno, *Rheologica Acta*, **26**, 172 (1987).

23. L. E. Kosinski and J. M. Caruthers, *Rheologica Acta*, **25**, 153 (1986).
24. S. C. Tsai and B. Viers, *J. Rheology*, **31**, 483 (1987).
25. S. Onogi, T. Matsumoto and Y. Warashina, *Trans. Soc. Rheol.*, **17**, 175 (1973).
26. T. A. Strivens, *Colloid and Polym. Sci.*, **261**, 74 (1983).
27. G. N. Choi and I. M. Krieger, *J. Colloid and Interface Sci.*, **113**, 101 (1986).
28. D. W. Meitz, L. Yen, G. C. Berry and H. Markovitz, *J. Rheology*, **32**, 309 (1988).
29. R. T. Mifflin and W. R. Schowalter, *AIChE Journal*, **34**, 1839 (1988).
30. J. Mewis, W. J. Frith, T. A. Strivens and W. B. Russel, *AIChE Journal*, **35**, 415 (1989).
31. D. Zou, V. Derlich, K. Gandhi, M. Park, L. Sun, D. Kriz, Y. D. Lee, G. Kim, J. J. Aklonis and R. Salovey, *J. Polym. Sci., Part A: Polym. Chem.*, **28**, 1909 (1990).
32. D. Zou, S. Ma, R. Guan, M. Park, L. Sun, J. J. Aklonis and R. Salovey, *J. Polym. Sci., Part A: Polym. Chem.*, in press.
33. K. Gandhi, M. Park, L. Sun, D. Zou, C. X. Li, Y. D. Lee, J. J. Aklonis and R. Salovey, *J. Polym. Sci., Part B: Polym. Phys.*, **28**, 2707 (1990).
34. M. M. Coleman, C. J. Serman, D. E. Bhagwagar and P. C. Painter, *Polymer*, **31**, 1187 (1990).
35. N. Casson, in *Rheology of Disperse Systems*, Edited by C. C. Mills, Pergamon Press, London (1959) page 84.
36. T. Matsumoto, A. Takashima, T. Masuda and S. Onogi, *Trans. Soc. Rheol.*, **14**, 617 (1970).
37. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd Edition, John Wiley, New York (1980), pages 41-43.
38. W. P. Cox and E. H. Merz, *J. Polym. Sci.*, **28**, 619 (1958).
39. H. C. Booij, P. Leblans, J. Palmen and G. Tiemersma-Thoone, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 1703 (1983).
40. W. M. Kulicke and R. S. Porter, *Rheol. Acta*, **19**, 601 (1980).
41. R. B. Bird, R. C. Armstrong and O. Hassager, *Dynamics of Polymeric Liquids*, Volume 1, 2nd Edition, John Wiley, New York (1987), page 150.
42. T. Kitano, T. Nishimura, T. Kataoka and T. Sakai, *Rheol. Acta*, **19**, 671 (1980).
43. S. Venkatraman, M. Okano and A. Nixon, *Polym Eng. Sci.*, **30**, 308 (1990).

44. G. C. Berry and T. G. Fox, *Adv. Polym. Sci.*, **5**, 251 (1968).
45. Reference 35, page 244; pages 374-379.
46. T. G. Fox and V. R. Allen, *J. Chem. Phys.*, **41**, 344 (1964).

LIST OF FIGURES

1. Steady shear viscosity (η) at 200°C and at several shear rates ($\dot{\gamma}$) of PS filled with 20% of crosslinked polymer beads.

- O pure PS matrix
- × with PS beads
- * with PMMA beads
- + with PEMA beads
- with PBMA beads

2. Storage modulus (G') at several frequencies (f) from dynamic mechanical analysis of PS composites from Figure 1.

3. Loss modulus (G'') at several frequencies (f) from dynamic mechanical analysis of PS composites from Figure 1.

4. Steady shear viscosity (η) at 200°C and at several shear rates ($\dot{\gamma}$) of PMMA filled with 20% of crosslinked polymer beads.

- O pure PMMA matrix
- × with PS beads
- * with PMMA beads
- + with PEMA beads
- with PBMA beads

5. Storage modulus (G') at several frequencies (f) from dynamic mechanical analysis of PMMA composites from Figure 4.

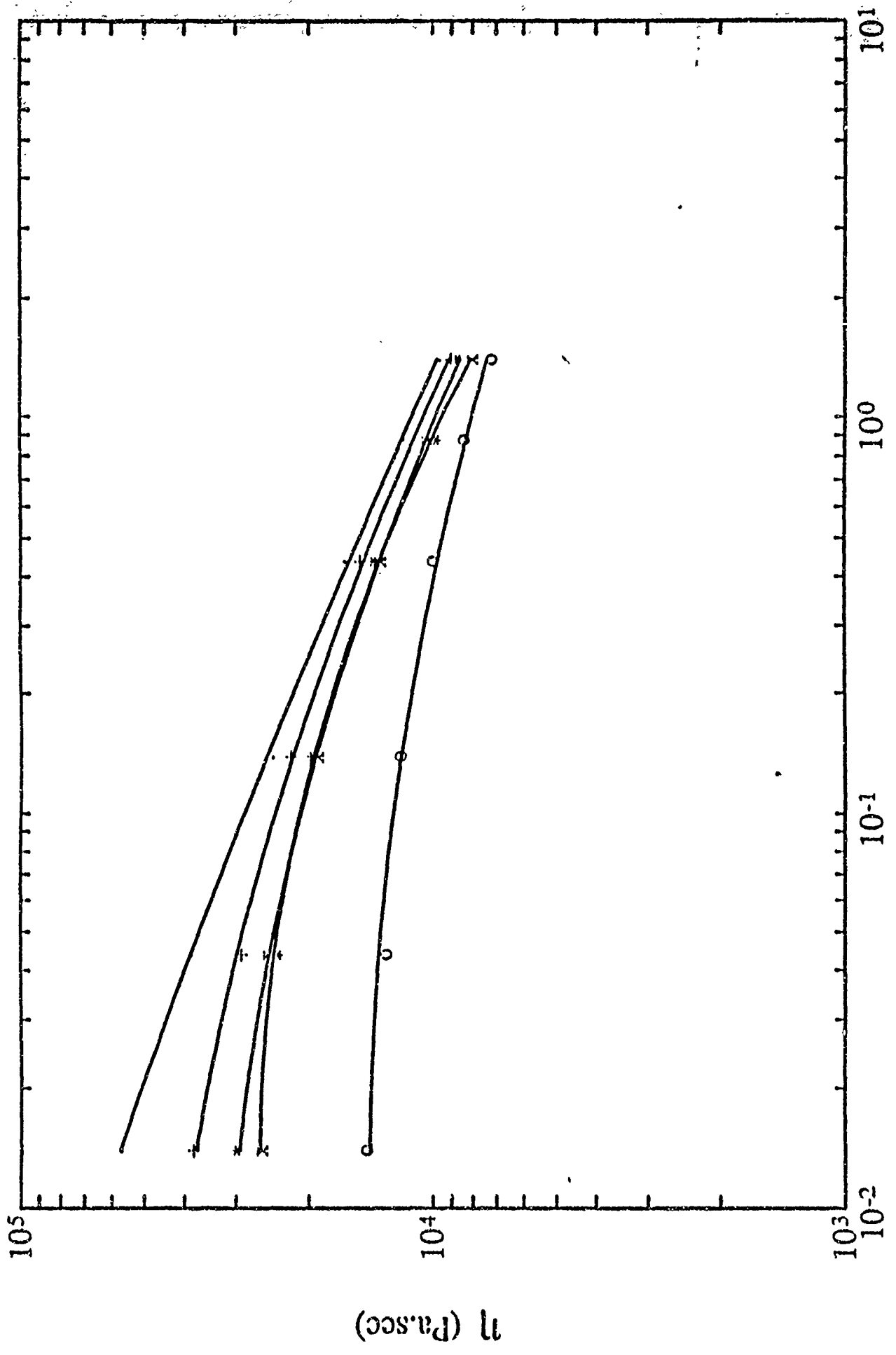
6. Loss modulus (G'') at several frequencies (f) from dynamic mechanical analysis of PMMA composites from Figure 4.
7. Steady shear viscosity (η) at 150°C and at several shear rates ($\dot{\gamma}$) of PBMA filled with 20% of crosslinked polymer beads.
 - pure PBMA matrix
 - × with PS beads
 - * with PMMA beads
 - with PBMA beads
8. Storage modulus (G') at several frequencies (f) from dynamic mechanical analysis of PBMA composites from Figure 7.
9. Loss modulus (G'') at several frequencies (f) from dynamic mechanical analysis of PBMA composites from Figure 7.
10. Steady shear viscosity (η) at 200°C and at several shear rates ($\dot{\gamma}$) of PMMA filled with various concentrations of crosslinked PS beads (2% DVB).
 - pure PMMA matrix
 - × 10 wt% of beads
 - * 20 wt% of beads
 - + 30 wt% of beads
 - 40 wt% of beads
11. Storage modulus (G') at several frequencies (f) from dynamic mechanical analysis of PMMA composites with PS beads from Figure 10.
12. Loss modulus (G'') at several frequencies (f) from dynamic mechanical analysis of PMMA composites with PS beads from Figure 10.

13. Steady shear viscosity (η) at 200°C and at several shear rates ($\dot{\gamma}$) of PMMA filled with various concentrations of crosslinked PMMA beads (2% EDGMA).

- pure PMMA matrix
- × 10 wt% of beads
- * 20 wt% of beads
- + 30 wt% of beads
- 40 wt% of beads

14. Storage modulus (G') at several frequencies (f) from dynamic mechanical analysis of PMMA composites with PMMA beads from Figure 13.

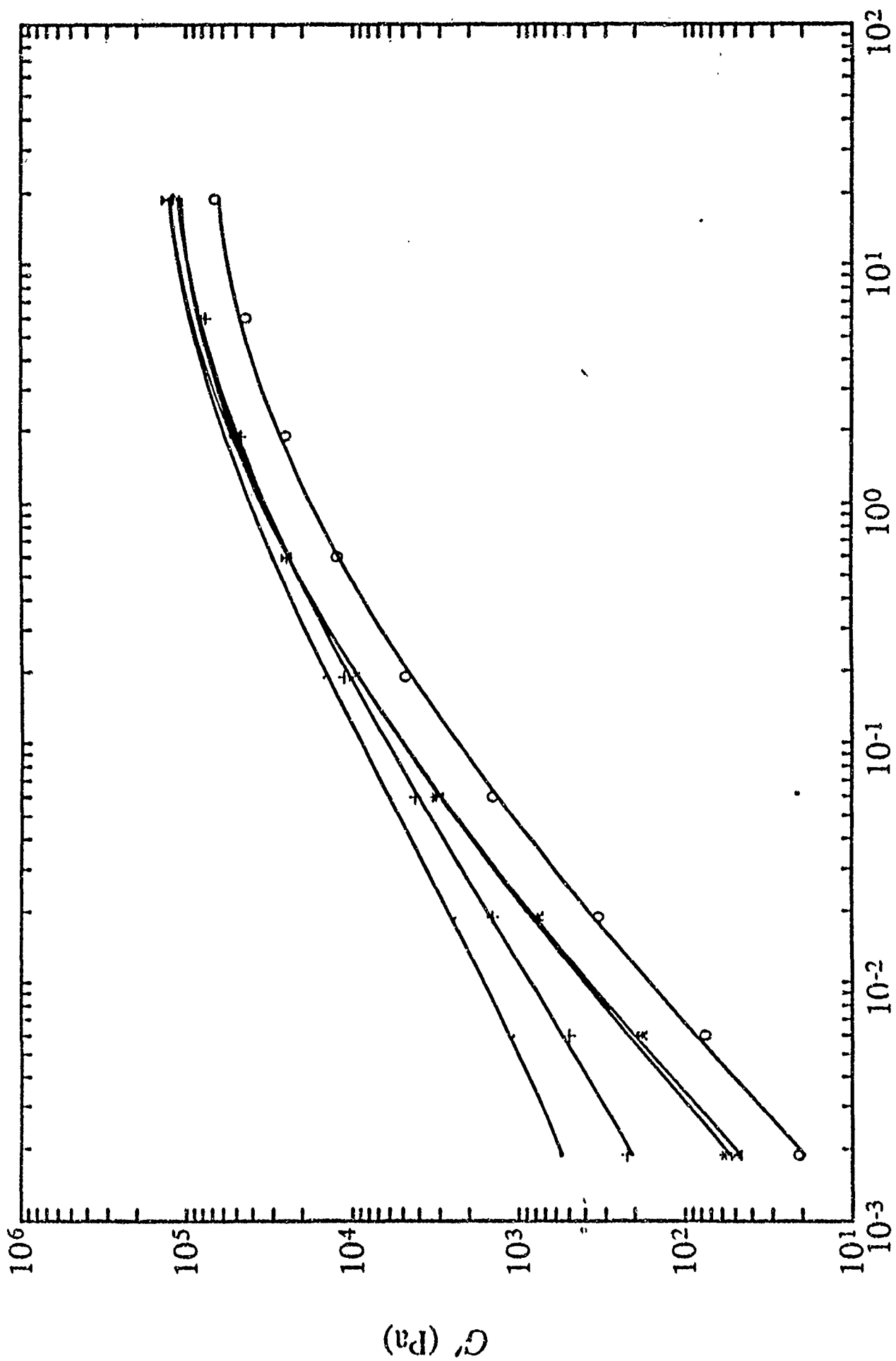
15. Loss modulus (G'') at several frequencies (f) from dynamic mechanical analysis of PMMA composites with PMMA beads from Figure 13.



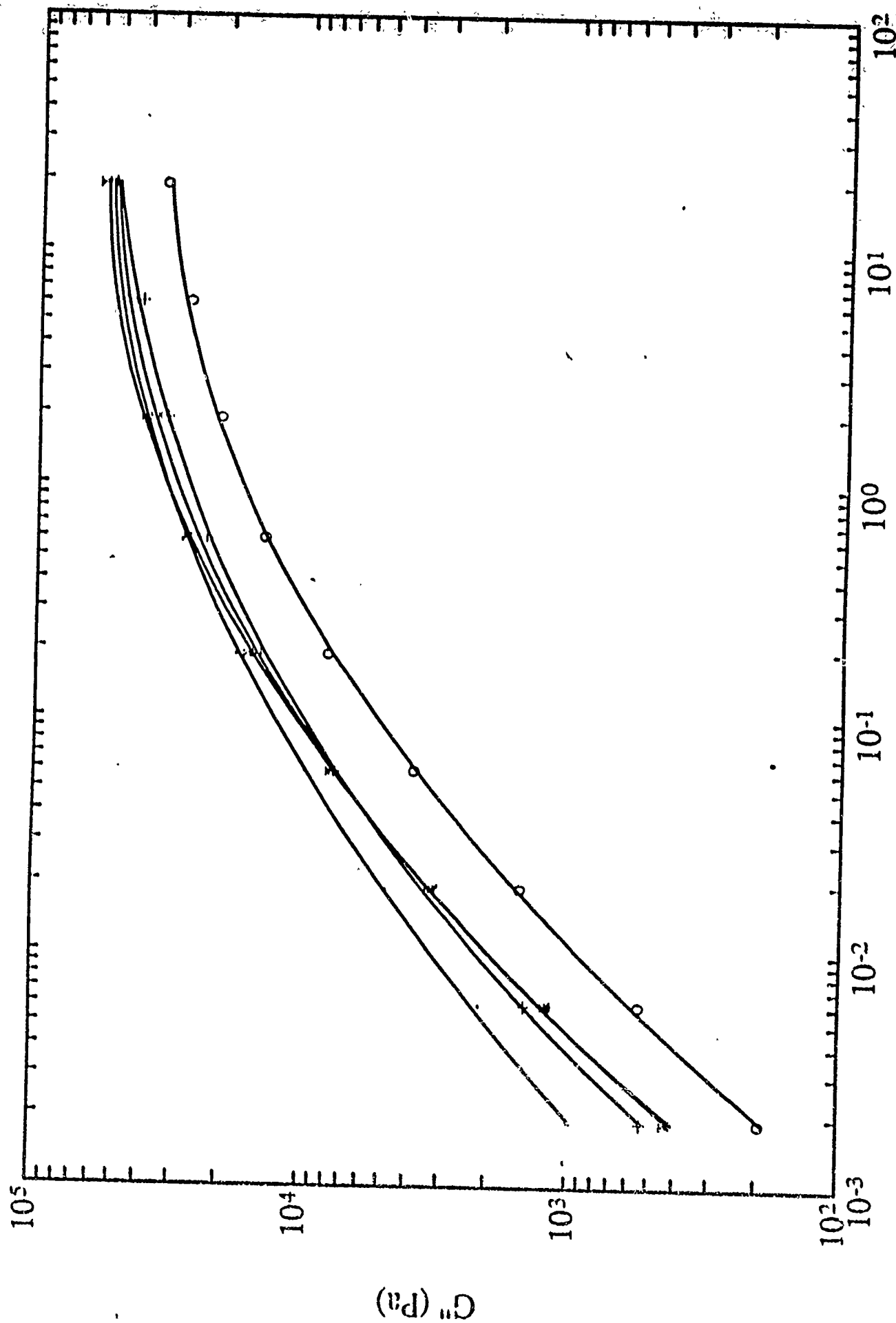
$\dot{\gamma}$ (1/sec)

FIGURE 1

η (Pa.s)

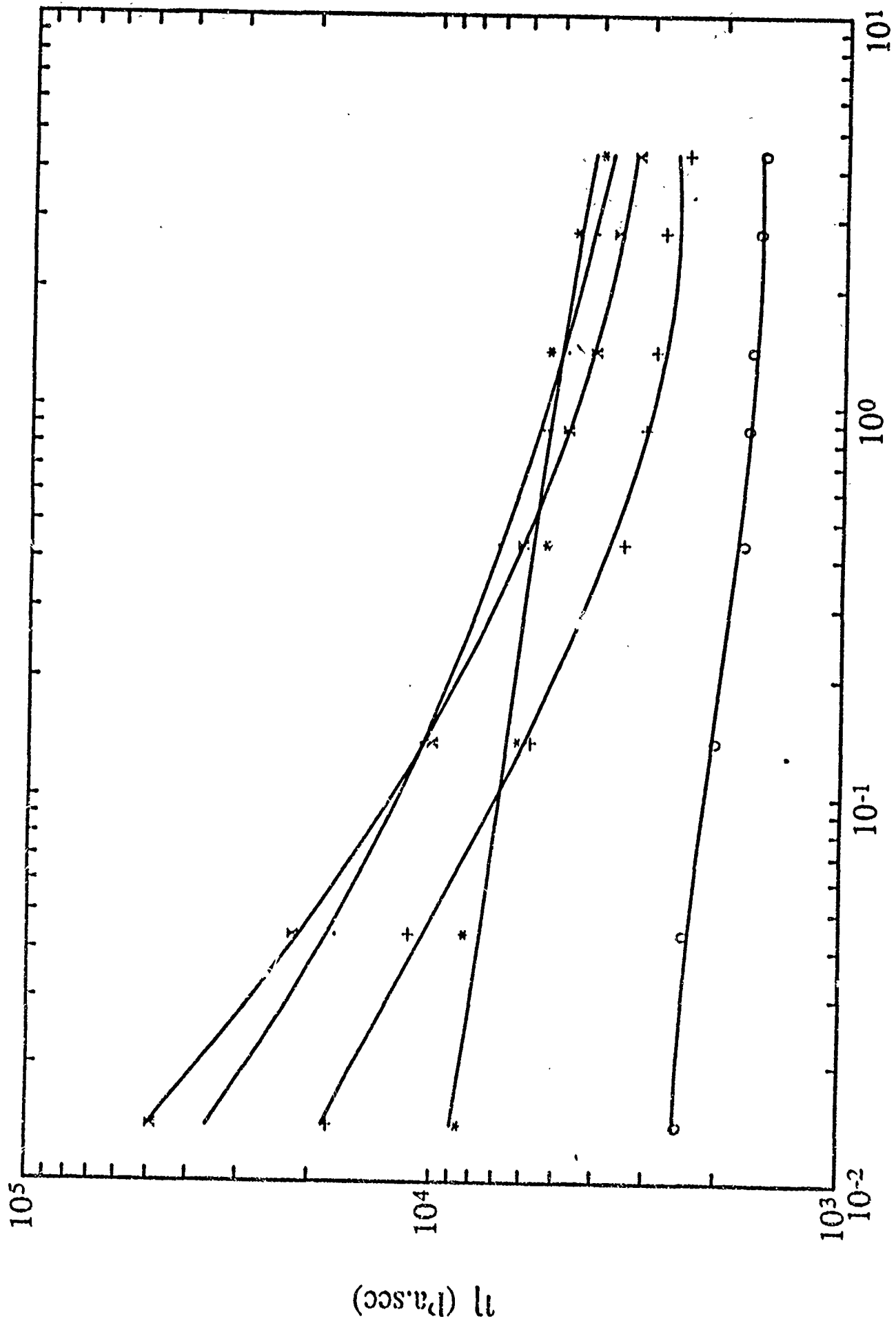


f (Hz)
FIGURE 2



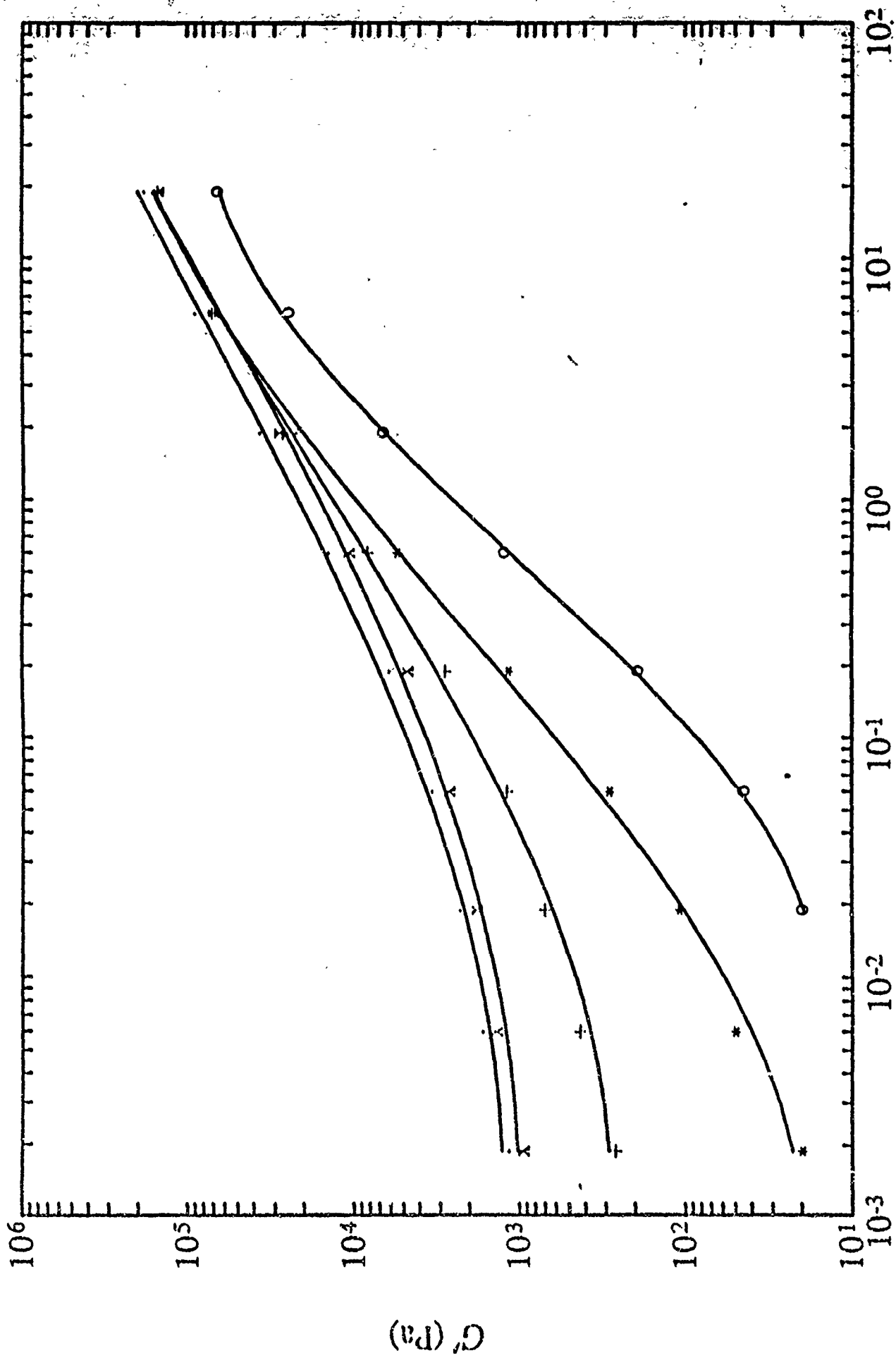
f (Hz)

FIGURE 3



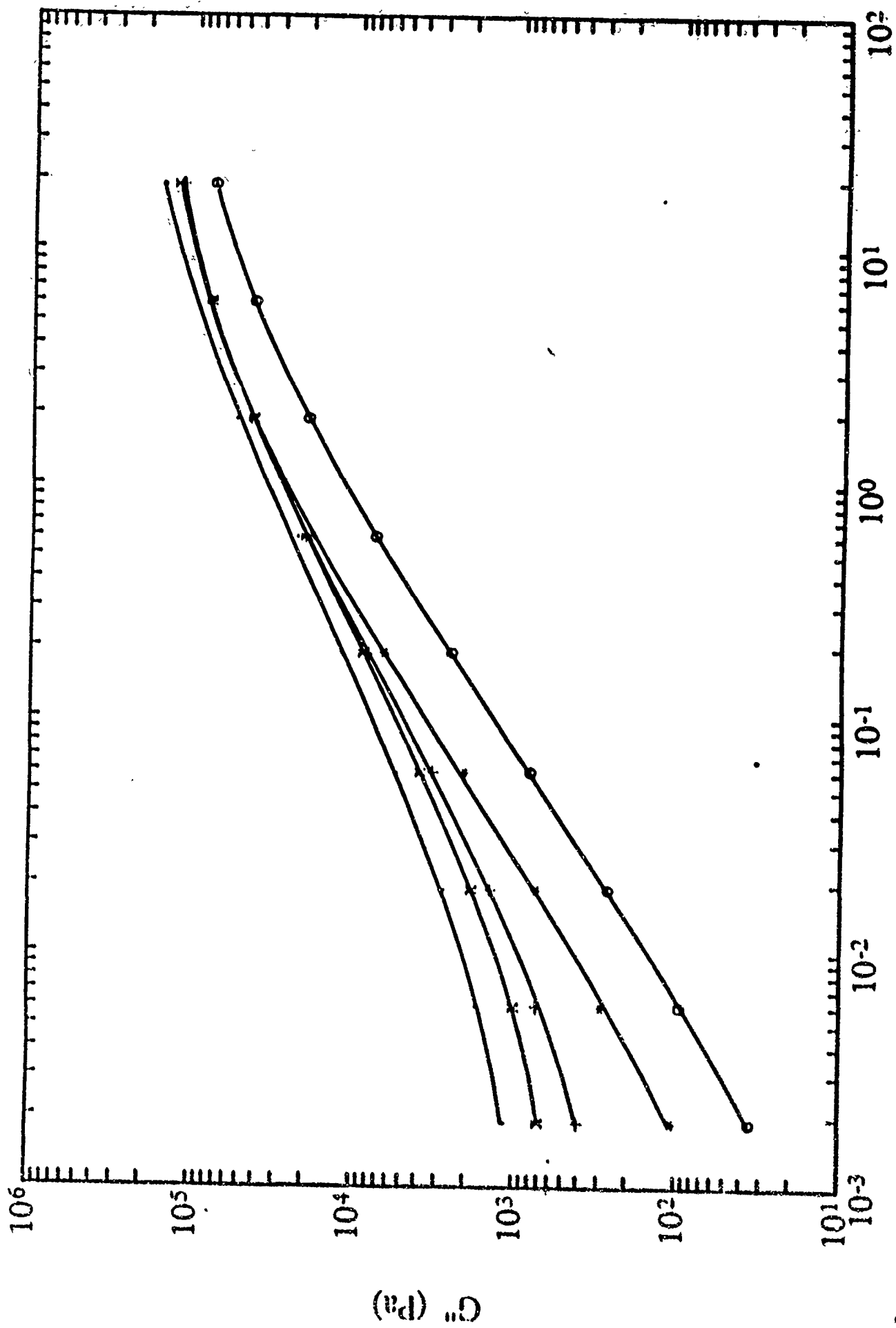
$\dot{\gamma}$ (1/sec)

FIGURE 4

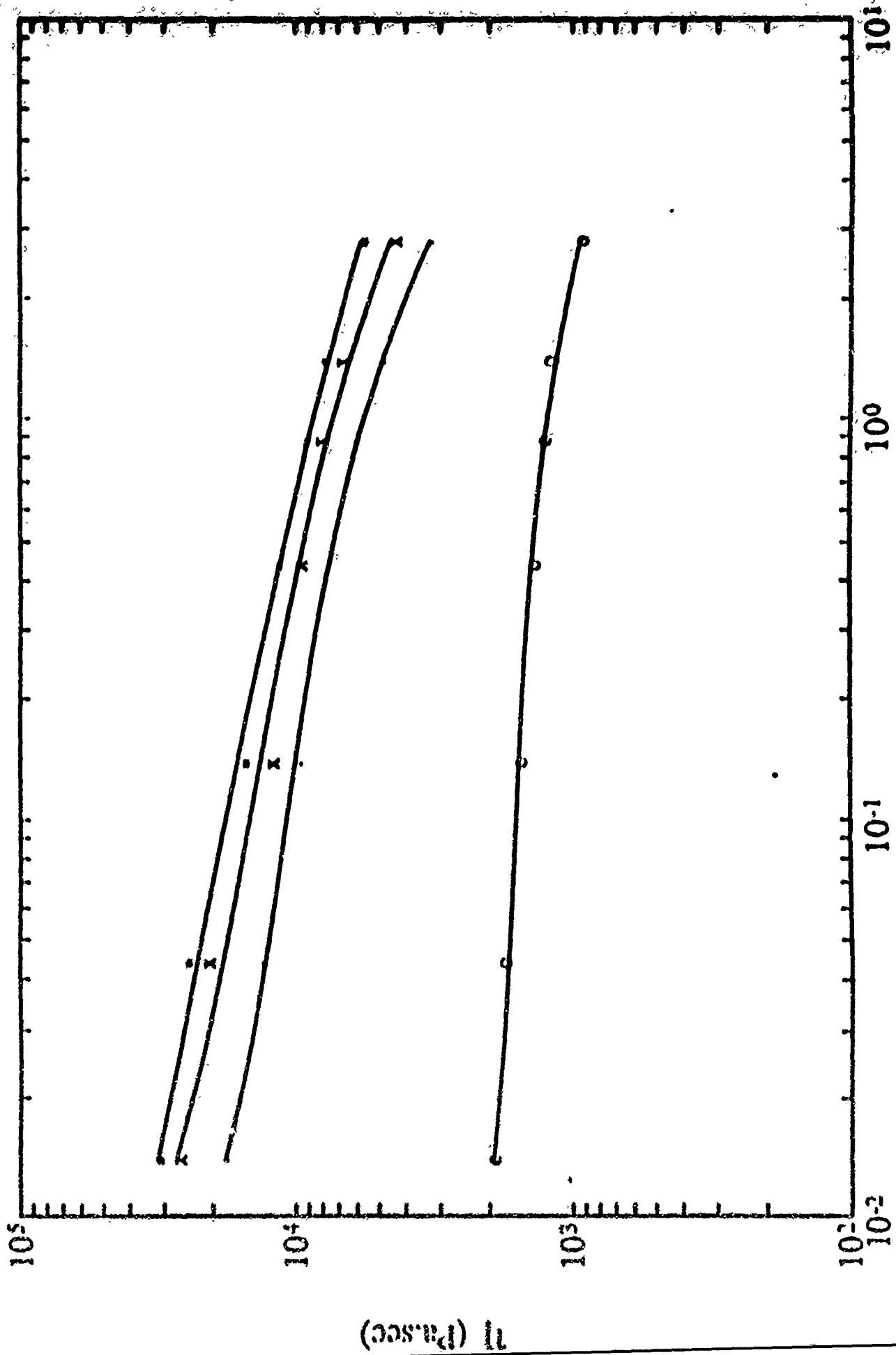


f (Hz)

FIGURE 5

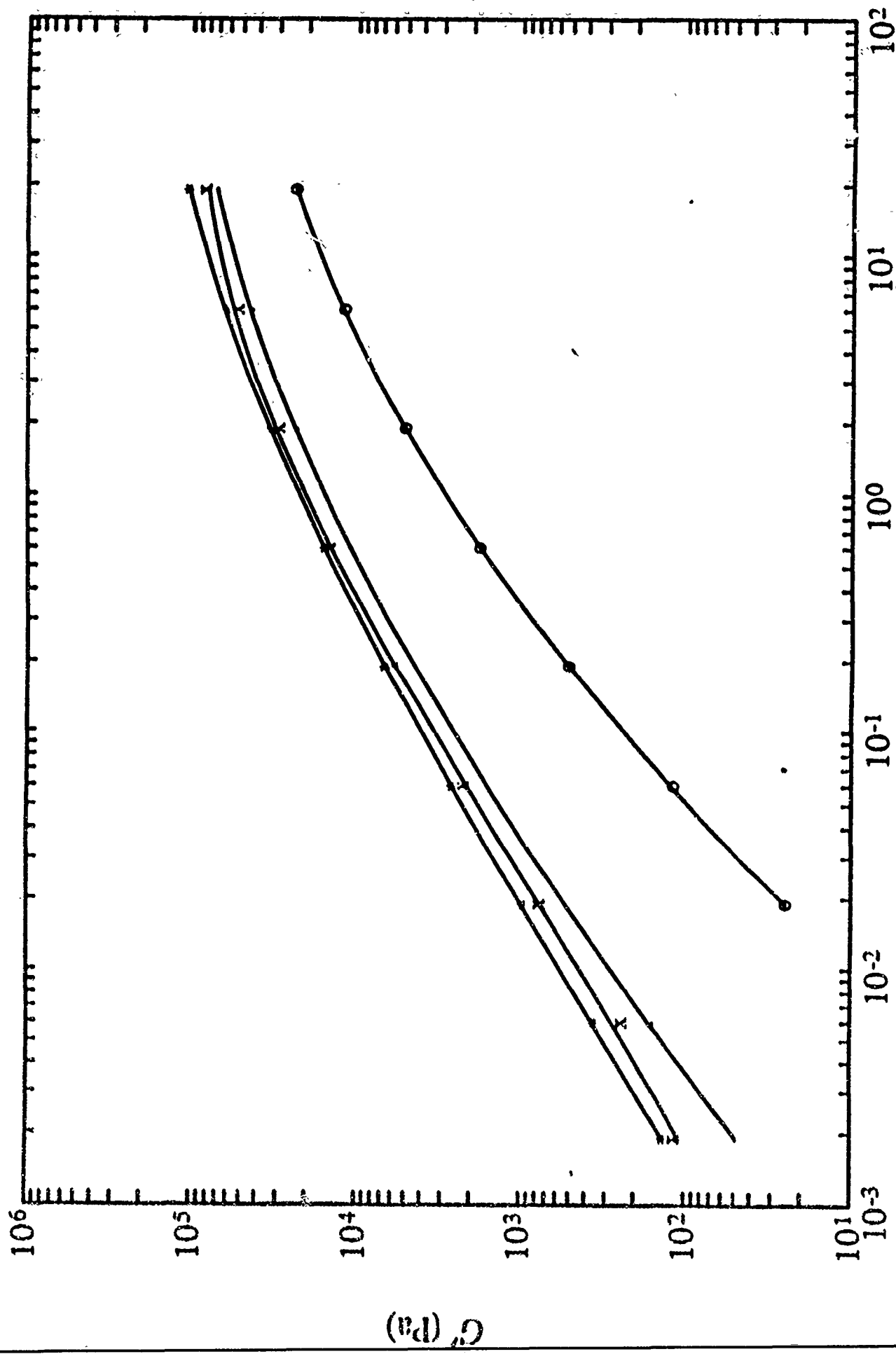


f (Hz)
FIGURE 6



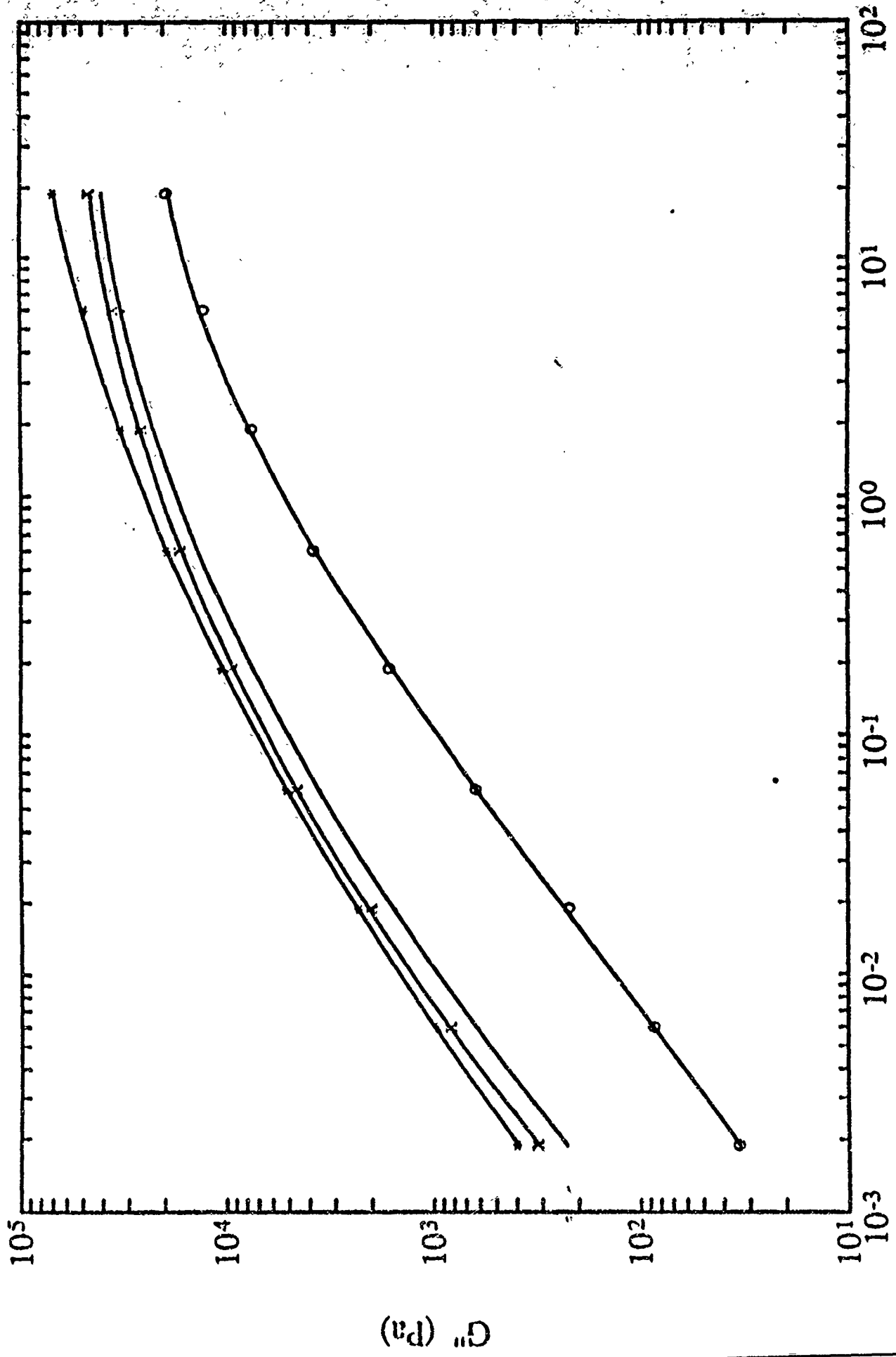
$\dot{\gamma}$ (1/sec)

FIGURE 7



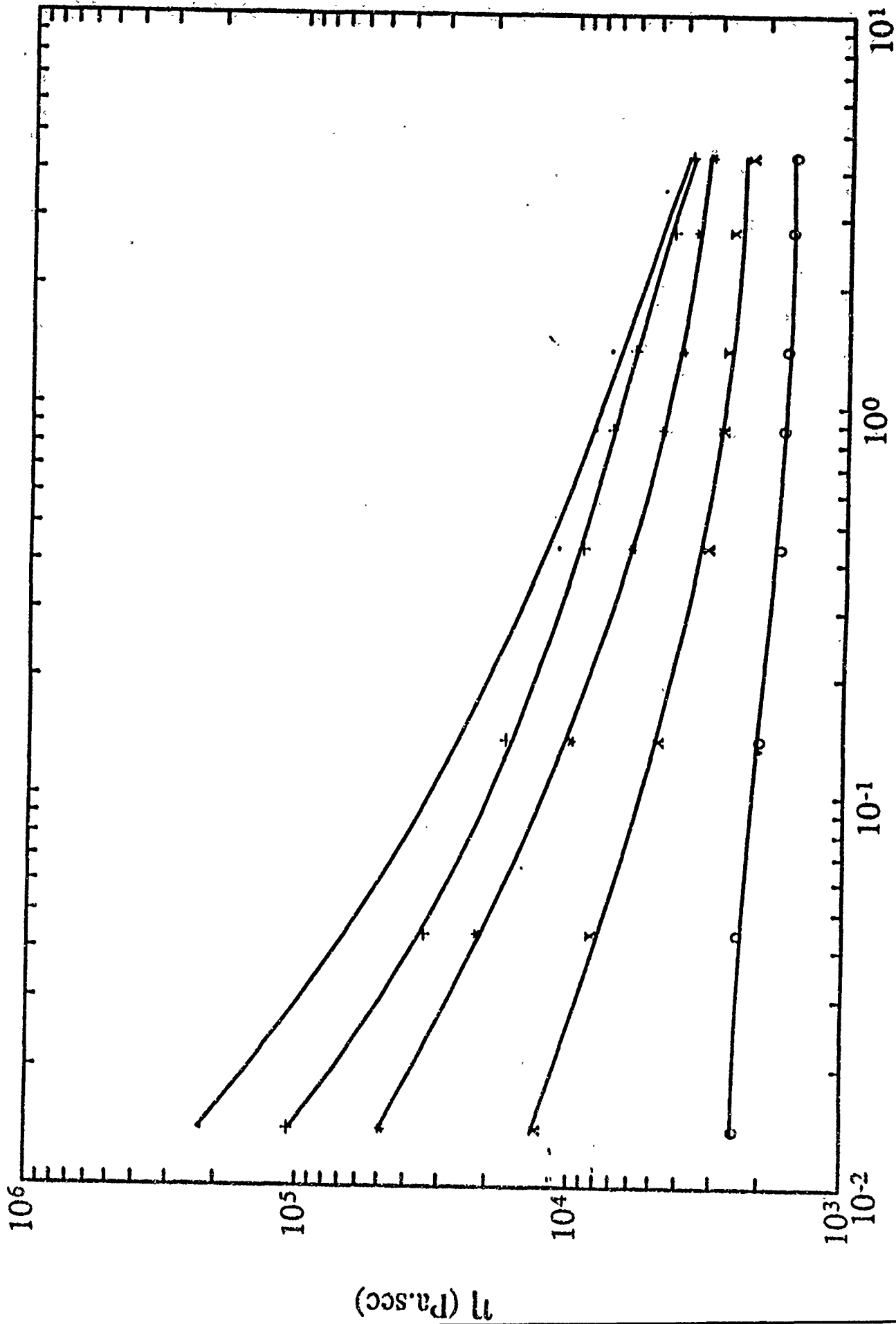
f (Hz)

FIGURE 8



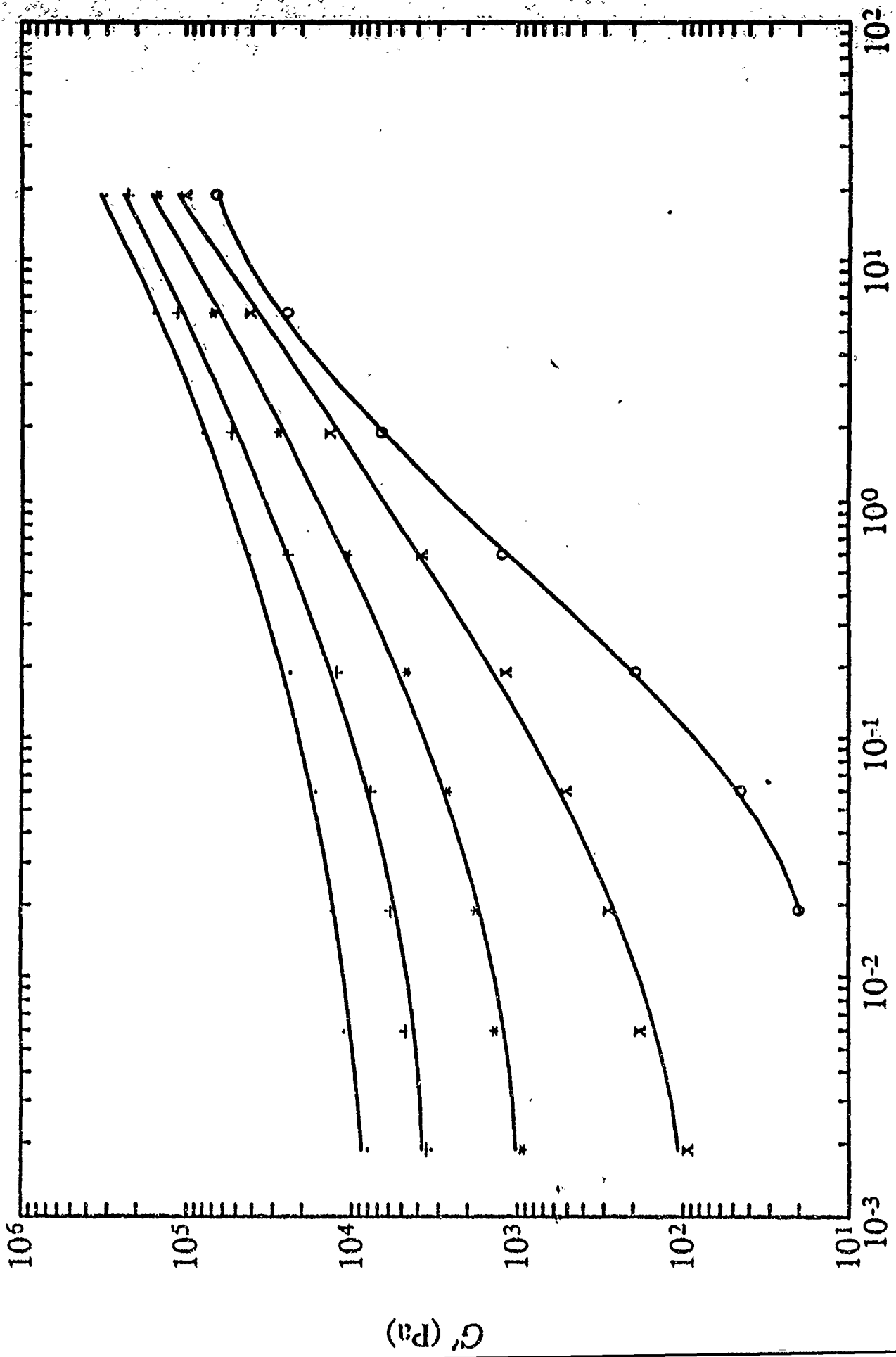
f (Hz)

FIGURE 9



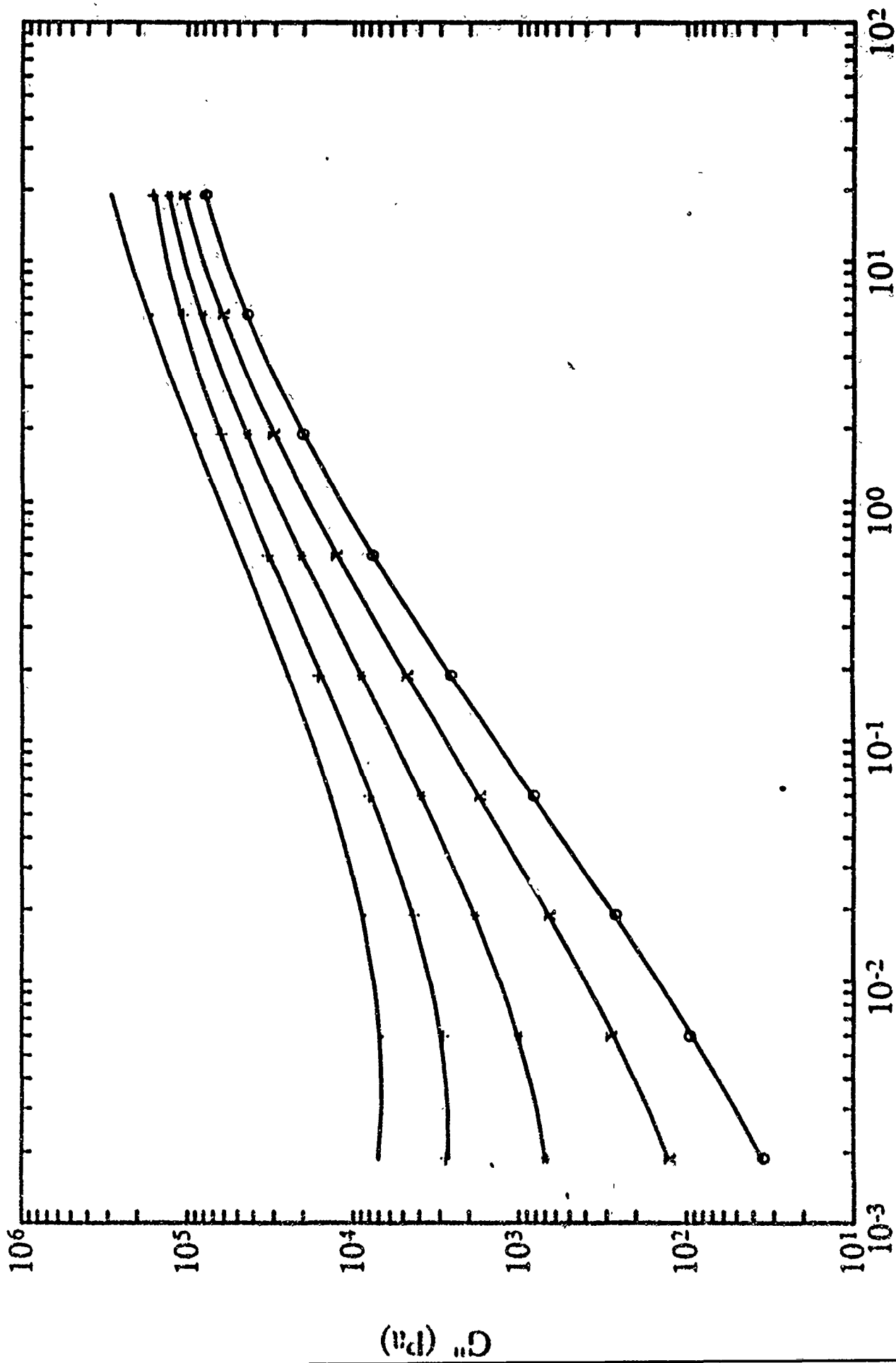
$\dot{\gamma}$ (1/sec)

FIGURE 10

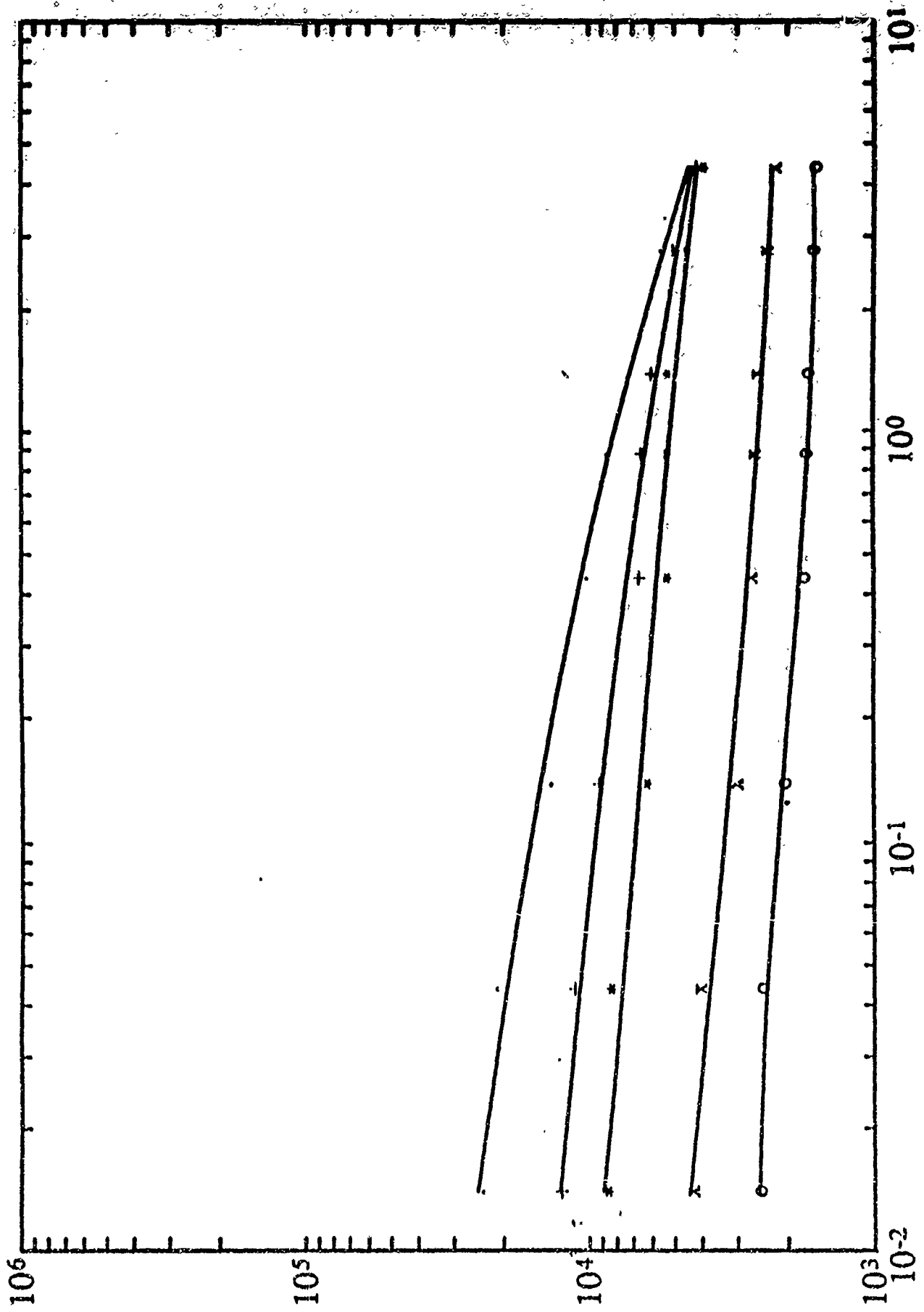


f (Hz)

FIGURE 11

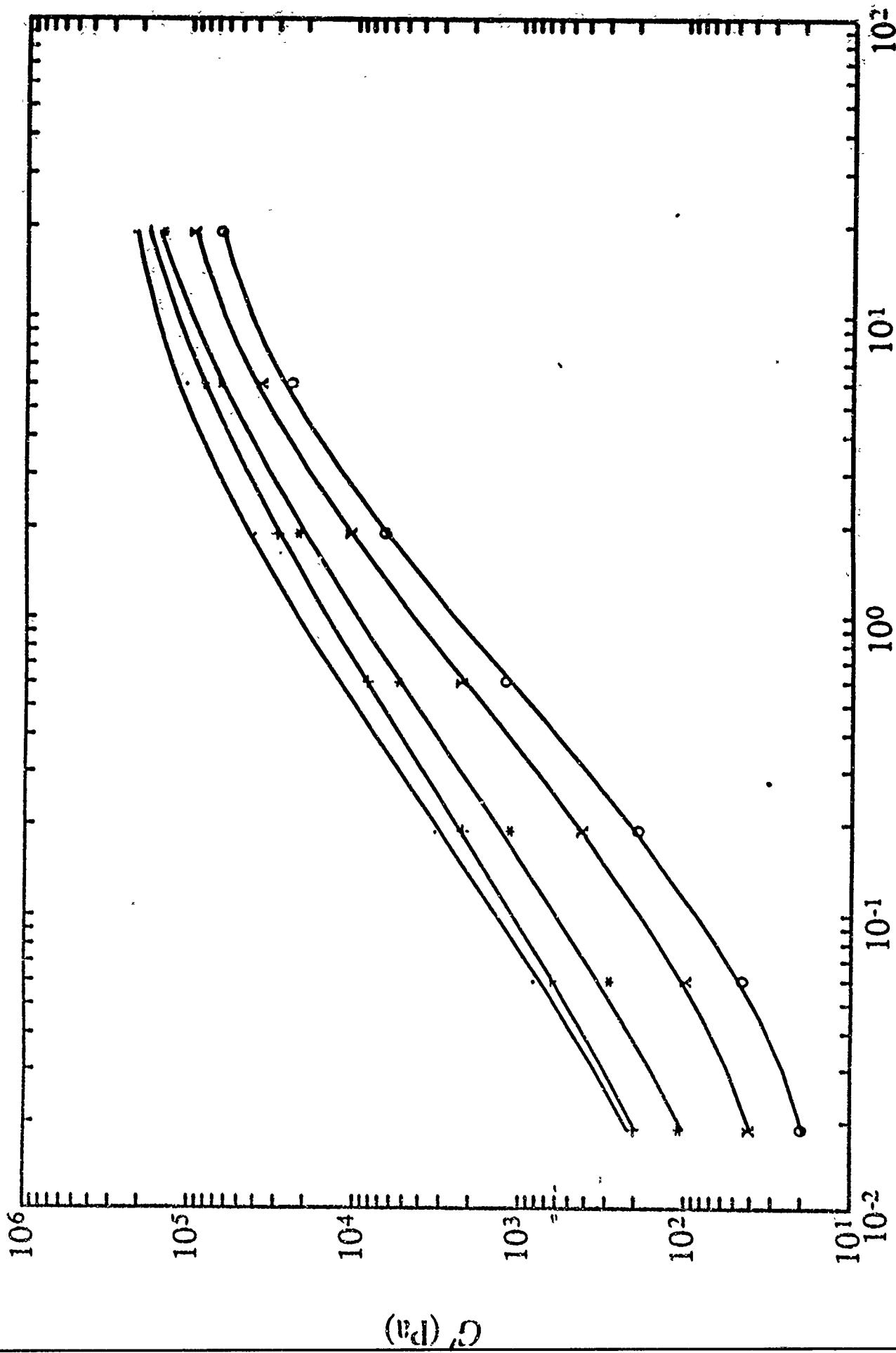


f (Hz)
FIGURE 12



$\dot{\gamma}$ (1/sec)

FIGURE 13



f (Hz)
FIGURE 14

JUN 11 1951

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2) *
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia 22217-5000

← glossy photos

Dr. Richard W. Drisko (1)
Naval Civil Engineering
Laboratory
Code L52
Port Hueneme, CA 93043

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Harold H. Singerman (1)
David Taylor Research Center
Code 283
Annapolis, MD 21402-5067

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Weapons Center
China Lake, CA 93555-6001

Chief of Naval Research (1)
Special Assistant for Marine
Corps Matters
Code 00MC
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Eugene C. Fischer (1)
Code 2840
David Taylor Research Center
Annapolis, MD 21402-5067

← glossy photos

Defense Technical Information
Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

Dr. Elek Lindner (1)
Naval Ocean Systems Center
Code 52
San Diego, CA 92152-5000

Commanding Officer (1)
Naval Weapons Support Center
Dr. Bernard E. Doua
Crane, Indiana 47522-5050

* Number of copies to forward

ABSTRACT DISTRIBUTION LIST

JUN 11 1991

Dr. John J. Aklonis
Dept. of Chemistry
Univ. of So. California
Los Angeles, CA 90089

Dr. Ali S. Argon
Mechanical Engineering Dept.
Massachusetts Inst. of Techn.
Cambridge, MA 02139

Dr. William Doane
Liquid Crystal Institute
Kent State University
Kent, OH 44242

Dr. James Economy
Mat. Sci. & Eng. Dept
University of Illinois
Urbana, IL 61820-6219

Dr. Alan D. MacDiarmid
Department of Chemistry
University of Pennsylvania
Philadelphia, PA 19104

Dr. Charles L. McCormick
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, MS 39046

Dr. Edward T. Samulski
Dept. of Chemistry
Univ. of North Carolina
Chapel Hill, NC 27599-3290

Dr. William P. Weber
Dept. of Chemistry
Univ. of Southern Calif.
Los Angeles, CA 90089-1661

Dr. Martin Pomerantz
Department of Chemistry
Univ. of Texas at Arlington
Box 19065
Arlington, TX 76019-0065

JUN 11 1951

Dr. Ronald Salovey
Dept. of Chem. Engineering
Univ. of Southern California
Los Angeles, CA 90089

Dr. Jerry-i. Scheinbeim
Dept. of Mech. & Mater. Sci.
Rutgers University
Piscataway, NJ 08854