

104
5

STRUCTURE-PROPERTY BEHAVIOR OF ELASTOMERIC TELECHELIC
IONOMERS IN BULK AND SOLUTION

by

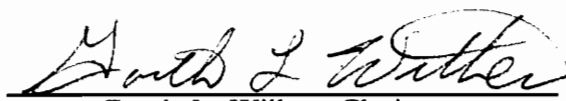
Martin Ray Tant_{//}

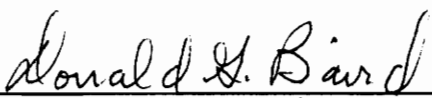
Dissertation submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

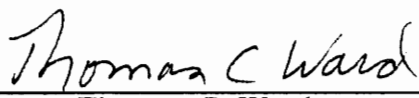
in

Chemical Engineering

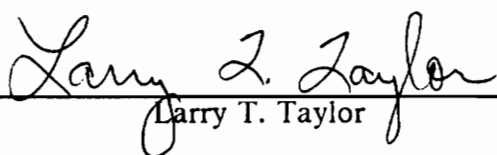
APPROVED:


Garth L. Wilkes, Chairman


Donald G. Baird


Thomas C. Ward


James E. McGrath


Larry T. Taylor

September 1986

Blacksburg, Virginia

C-2

LD
5655
V856
1986
T369
C.2

STRUCTURE-PROPERTY BEHAVIOR OF ELASTOMERIC TELECHELIC IONOMERS IN BULK AND SOLUTION

by

Martin Ray Tant

Garth L. Wilkes, Chairman

Chemical Engineering

(ABSTRACT)

The structure-property behavior of two types of elastomeric telechelic ionomers has been investigated. Sulfonated polyisobutylene telechelic ionomers were studied in both bulk and solution. The bulk mechanical properties of carboxylated polyisoprene telechelic ionomers were also investigated.

The sulfonated polyisobutylene telechelic ionomers are available in three different molecular architectures - linear monofunctional, linear difunctional, and three-arm star trifunctional. These materials, which had previously been neutralized only with monovalent and divalent cations, were neutralized with cerium(III) and lanthanum(III). These trivalent cations resulted in a material with improved network stability over those materials previously studied. Long term stress relaxation and creep experiments revealed that at short times the networks are stable while the materials flow after about one week of relaxation.

Studies of the solution behavior of the sulfonated polyisobutylene telechelic ionomers concerned dilute solution viscometric behavior in nonpolar solvents and nonpolar-polar solvent mixtures as well as the viscoelastic behavior of more concentrated solutions in nonpolar solvents. Gelation was observed in nonpolar solvents at concentrations as low as 1-2 g/dl. The gelation concentration is dependent upon molecular architecture, molecular weight, neutralizing cation type, and excess neutralizing

agent. The viscosity of these ionomers in nonpolar-polar solvent mixtures may increase with increasing temperature due to the temperature -dependent equilibrium between the ionic groups, the polar cosolvent, and the nonpolar solvent. More concentrated solutions or gels in nonpolar solvents display a unique viscoelastic behavior which is very dependent upon architecture, molecular weight, and neutralizing cation. Solutions of ionomers (5 g/dl) neutralized with zinc display a low-frequency viscous region and a high-frequency elastic region at room temperature. Solutions of ionomers neutralized with more ionic cations display an elastic response over essentially the entire frequency range. Storage and loss modulus curves obtained at different temperatures do not superpose, and these solutions are thus thermorheologically complex.

The bulk mechanical properties of carboxylated polyisoprene telechelic (linear) ionomers were studied. For materials neutralized with Group IA or IIA metals, resistance to flow was found to increase with decreasing ionic radius. The zinc-neutralized material flowed with little resistance, while the nickel-neutralized material exhibited the best elastomeric characteristics. Materials neutralized with titanium(IV) required a fourfold stoichiometric excess to reach maximum strength due to the difference in neutralization pathway. An amine-terminated polybutadiene crosslinked with copper(II) chloride displayed greater strength and network stability than any of the carboxylated polyisoprene telechelic ionomers.

To Martha

Acknowledgements

I would like to express my appreciation to Professor Garth L. Wilkes for serving as my major professor for both of my graduate degrees. His energetic approach to research is something that I can only strive to achieve. It has been a pleasure to work with him, and I look forward to our continuing friendship and professional association. Thanks are also extended to Professors D. G. Baird, T. C. Ward, J. E. McGrath, and L. T. Taylor for serving as committee members and for their willingness to discuss problems encountered during the course of the research.

Professor W. L. Conger, Head of the Department of Chemical Engineering, has been very supportive throughout the course of my graduate studies, and this support is greatly appreciated. I am also grateful to the Graduate School and the University for my selection as a Cunningham Dissertation Year Fellow for the 1985-86 academic year. Financial support from the American Chemical Society is also gratefully acknowledged.

Professor Roy L. Williams of the Department of Chemical Sciences at Old Dominion University spawned my interest in polymers and encouraged my interest in chemical engineering when some others did not. He even volunteered to teach an elective course in polymer science during my senior year after learning of my interest in polymers. I might have never reached this goal had I not received such strong encouragement at this early point in my education.

Although Professor J. B. Henderson of the Department of Mechanical Engineering and Applied Mechanics at the University of Rhode Island was not directly involved in my graduate education, he has had a strong influence on my approach to engineering

research. After working together for three years at the Naval Surface Weapons Center, we have continued our interaction during the past several years and have continued to publish joint papers concerning our work on polymer composites. I hope that we will be able to continue our interaction in the future.

Dr. Joo H. Song was very involved in this research, and did most of the experimental work on the carboxylated elastomeric telechelic ionomers. His contributions to the project are certainly appreciated. The experimental efforts of Dr. Raj Subramanian on the dynamic mechanical behavior of the ionomers are also gratefully acknowledged. Leonardo López was very helpful in introducing me to word processing so that I could produce this dissertation, and I appreciate his assistance.

I am fortunate to have parents who taught me the value of education by their own example, and who have always encouraged my interest in science and engineering. My parents-in-law, Mr. and Mrs. Bentley Hite, have also been very supportive of Martha and me throughout our graduate careers, and we certainly appreciate their devotion. Finally, without the love and support of my wife, Martha, none of this would have been possible.

Table of Contents

I. Introduction	1
II. Review of Previous Work	4
Structure of Ionomers	5
Chemical Structure	5
Morphological Structure	7
Mechanical/Viscoelastic Behavior of Ionomers	16
Behavior in the Glassy Region	17
Behavior in the Glass Transition Region	20
Behavior in the Rubbery Region	26
Sulfonated EPDM.	28
Carboxylated Elastomeric Telechelic Ionomers.	31
Sulfonated Polyisobutylene Telechelic Ionomers.	37
Carboxylated SBR.	39
Polyurethane Ionomers.	41
Behavior of Melts	43
Behavior of Blends	48
Rheological Behavior of Ionomer Solutions	52
Viscometric Behavior	53
Nonpolar solvents.	53
Polar solvents.	58
Nonpolar-polar solvent mixtures.	58
Dynamic Behavior	60
III. Purpose and Scope of Present Work	68
Bulk Structure and Properties of Sulfonated Polyisobutylene Telechelic Ionomers	68
Solution Behavior of Sulfonated Polyisobutylene Telechelic Ionomers	70
Bulk Properties of Carboxylated Elastomeric Telechelic Ionomers	72
IV. Experimental	73
Materials	73
Sulfonated Polyisobutylene Telechelic Ionomers	73
Carboxylated Elastomeric Telechelic Ionomers	77
Experimental Methods	78
Small Angle X-Ray Scattering (SAXS)	78
Mechanical Properties	78
Dynamic Mechanical Properties	79
Thermomechanical Analysis	79
Solution Viscometry	80
Solution Viscoelasticity	81
V. Results and Discussion	82
Structure and Properties of Sulfonated Polyisobutylene Telechelic Ionomers in Bulk	82

Bulk Structure	82
Long Term Stress Relaxation and Creep Behavior	86
Properties of Materials Neutralized with Elements of the Lanthanide Series	88
Dynamic Mechanical Behavior	95
Summary	103
Viscometric and Viscoelastic Behavior of Sulfonated Polyisobutylene Telechelic Ionomers in Solution	105
Viscometric Behavior of Dilute Solutions	105
Nonpolar Solvents	105
Nonpolar-Polar Solvent Mixtures	128
Viscoelastic Behavior of Concentrated Solutions	144
Summary	179
Mechanical and Viscoelastic Behavior of Carboxylated Elastomeric Telechelic Ionomers in Bulk	179
Effect of Molecular Weight and Cation Valence on Mechanical Properties	181
Effect of Monovalent and Divalent Cation Type on Mechanical Properties	192
Effect of Amines on Mechanical Properties of Nickel Neutralized Materials	204
Mechanical Properties of Materials Neutralized with Titanium	205
Mechanical Properties of Amine-Terminated Polybutadiene	217
Summary	221
VI. Conclusions	223
Bulk Structure and Properties of Sulfonated Polyisobutylene Telechelic Ionomers	223
Solution Behavior of Sulfonated Polyisobutylene Telechelic Ionomers	224
Bulk Properties of Carboxylated Elastomeric Telechelic Ionomers	226
VII. Recommendations for Further Study	228
Bulk Structure and Properties of Sulfonated Polyisobutylene Telechelic Ionomers	228
Solution Behavior of Sulfonated Polyisobutylene Telechelic Ionomers	229
Bulk Properties of Carboxylated Elastomeric Telechelic Ionomers	231
References	232

List of Illustrations

Figure 1. X-ray scattering curves of polyethylene-based materials	9
Figure 2. Schematic of MacKnight, Taggart, and Stein model	12
Figure 3. Schematic of Fujimura, Hashimoto, and Kawai model	14
Figure 4. Schematic of Yarusso and Cooper model	15
Figure 5. Plot of glass transition temperature vs. cq/a	19
Figure 6. Stress relaxation master and pseudomaster curves for six ionomers	23
Figure 7. Storage modulus G' vs. temperature for zinc sulfonate EPDM's	29
Figure 8. Dynamic behavior of carboxy-telechelic polybutadiene at 302K	33
Figure 9. G' master curves for carboxy-telechelic polyisoprene	35
Figure 10. Stress-strain behavior of sulfonated PIB telechelic ionomers	38
Figure 11. Stress-strain behavior of sulfonated PIB telechelic ionomers	40
Figure 12. G' vs. frequency for a polyester ionomer	44
Figure 13. G' vs. frequency for three-arm star trifunctional ionomer	46
Figure 14. G' vs. temperature for a 50/50 blend of polystyrene with poly(ethyl acrylate)	50
Figure 15. G' vs. temperature for a 50/50 blend of sulfonated polystyrene and poly(ethyl acrylate) containing vinylpyridine	51
Figure 16. Reduced viscosity vs. concentration of sulfonated PS in THF	54
Figure 17. Effect of neutralization with magnesium on relative viscosity of carboxy-telechelic polyisoprene	55
Figure 18. Effect of molecular weight on gelation behavior of carboxy-telechelic polyisoprene neutralized with magnesium	57
Figure 19. Reduced viscosity vs. concentration for sulfonated PS in DMF	59
Figure 20. Viscosity-temperature behavior of 3% and 18% polystyrene in xylene	61

Figure 21. Viscosity-temperature behavior of sulfonated polystyrene (1.98 mole %) in xylene/hexanol	62
Figure 22. G' and G'' vs. frequency for zinc sulfonated EPDM's	63
Figure 23. Predicted G' and G'' behavior for an ionomer gel	66
Figure 24. Chemical structures of the sulfonated polyisobutylene telechelic ionomers.	76
Figure 25. SAXS curves for linear difunctional ionomers	83
Figure 26. SAXS curves for three-arm star trifunctional ionomers	85
Figure 27. Stress relaxation and creep behavior of the T-14-K-X series	87
Figure 28. Comparison of networks formed by trifunctional ionomers neutralized with (a) divalent and (b) trivalent cations.	89
Figure 29. Stress-strain behavior of the D-6.5-X-0 series.	91
Figure 30. Stress relaxation and creep behavior of the D-6.5-X-0 series.	92
Figure 31. Stress-strain curves for the T-19 series.	93
Figure 32. Instantaneous set for T-19 materials in cyclic loading-unloading experiment.	94
Figure 33. Recovery of T-19 materials following 400% elongation for one week. ..	96
Figure 34. Effect of molecular architecture on G' and $\tan \delta$ at a relatively constant molecular weight of 11000-12000.	98
Figure 35. Dynamic mechanical behavior of linear polyisobutylene	99
Figure 36. Effect of molecular weight on G' and $\tan \delta$ of trifunctional ionomers. .	101
Figure 37. Effect of cation type on G' and $\tan \delta$ for the D-6.5 series.	102
Figure 38. Effect of excess cation on G' and $\tan \delta$ for the T-14-K series.	104
Figure 39. Effect of sulfonation and KOH neutralization upon relative viscosity for D-12-K-0 in hexane.	107
Figure 40. Effect of sulfonation and KOH neutralization upon relative viscosity for T-11-K-0 in hexane.	109
Figure 41. Apparent degree of polymerization required to produce observed viscosity for D-6.5-K-0 and D-12-K-0 in hexane.	112

Figure 42. Comparison of chain extension and cyclic structure formation for linear difunctional ionomer.	113
Figure 43. Effect of molecular architecture upon viscosity at an approximately constant molecular weight of 11000-12000.	114
Figure 44. Schematic of ion association resulting in formation of gel structure with similar crosslink density	116
Figure 45. Gelation curves for D-12-K-0 and T-11-K-0 in hexane based on ionic concentration.	117
Figure 46. Effect of molecular weight upon the viscosity-concentration behavior of the three-arm star trifunctional ionomer.	121
Figure 47. Plot of log of gelation concentration vs. log of molecular weight for three-arm star trifunctional ionomers.	123
Figure 48. Effect of molecular weight upon the viscosity-concentration behavior for the linear difunctional ionomers.	124
Figure 49. Effect of neutralizing agent and excess neutralizing agent on viscosity behavior of D-6.5 in hexane.	126
Figure 50. Effect of neutralizing agent and excess neutralizing agent on viscosity behavior of D-12 in hexane.	127
Figure 51. Viscosity behavior of T-11-K-0 in hexane and THF.	129
Figure 52. Effect of temperature on relative viscosity of D-12-K-0 in decalin. ...	130
Figure 53. Effect of temperature on kinematic viscosity of T-11-K-0 in 2% hexanol-98% decalin.	132
Figure 54. Effect of temperature on relative viscosity of T-11-K-0 in 2% hexanol-98% decalin.	133
Figure 55. Effect of temperature on kinematic viscosity of D-12-K-0 at a concentration of 1.5 g/dl in hexanol/decalin.	135
Figure 56. Effect of temperature on relative viscosity of D-12-K-0 at a concentration of 1.5 g/dl in hexanol/decalin.	136
Figure 57. Effect of temperature on kinematic viscosity of D-12-K-0 at a concentration of 2.0 g/dl in hexanol/decalin.	137
Figure 58. Effect of temperature on relative viscosity of D-12-K-0 at a concentration of 2.0 g/dl in hexanol/decalin.	138
Figure 59. Effect of hexanol content on relative viscosity of D-12-K-0 at a concentration 2.0 g/dl.	139

Figure 60. Effect of temperature on kinematic viscosity of D-6.5-K-0 and D-12-K-0 at 2.0 g/dl in 1% hexanol-99% decalin.	141
Figure 61. Effect of temperature on relative viscosity of D-6.5-K-0 and D-12-K-0 at 2.0 g/dl in 1% hexanol-99% decalin.	142
Figure 62. Time dependent relative viscosity of D-6.5-K-0 in 1% hexanol-99% decalin	143
Figure 63. Dynamic behavior of D-12-ZnAc-100 in decalin at 28°C.	145
Figure 64. Dynamic behavior of T-11.3-ZnAc-100 in decalin at 27°C.	148
Figure 65. Dynamic behavior of linear polyisobutylene in decalin at 27°C	150
Figure 66. Effect of cation type upon G' of D-6.5 ionomer in decalin at 5 g/dl. ..	152
Figure 67. Effect of molecular weight upon dynamic behavior of linear difunctional ionomers in decalin at 5 g/dl.	153
Figure 68. Effect of molecular weight upon G' of three-arm star trifunctional species in decalin at 2.5 g/dl.	155
Figure 69. Effect of concentration upon G' of D-6.5-K-0 in decalin at 27-31°C. .	156
Figure 70. Plot of log of plateau modulus vs. log of concentration for D-6.5-K-0 in decalin.	158
Figure 71. Effect of temperature upon G' of D-12-K-0 in decalin at 10 g/dl.	159
Figure 72. Effect of temperature upon G'' of D-12-K-0 in decalin at 10 g/dl.	160
Figure 73. Effect of temperature upon G' of T-10.6-K-0 in decalin at 2.5 g/dl. ...	161
Figure 74. Effect of temperature upon G'' of T-10.6-K-0 in decalin at 2.5 g/dl. ..	162
Figure 75. Dynamic behavior of D-6.5-K-0 in 100N oil (10 g/dl) at 31°C.	164
Figure 76. Dynamic behavior of D-6.5-K-0 in 100N oil (10 g/dl) at 50°C.	165
Figure 77. Dynamic behavior of D-6.5-K-0 in 100N oil (10 g/dl) at 70°C.	166
Figure 78. Dynamic behavior of D-6.5-K-0 in 100N oil (10 g/dl) at 100°C.	167
Figure 79. Effect of temperature upon G' of D-6.5-K-0 in 100N oil (10 g/dl). ...	168
Figure 80. Effect of temperature upon G'' of D-6.5-K-0 in 100N oil (10 g/dl). ...	169
Figure 81. Plot of log shift factor vs. $1/T$ for D-6.5-K-0 in 100N oil (10 g/dl). ...	171
Figure 82. Dynamic behavior of T-34-K-0 in 100N oil (5 g/dl) at 30°C.	173

Figure 83. Dynamic behavior of T-34-K-0 in 100N oil (5 g/dl) at 50°C.	174
Figure 84. Dynamic behavior of T-34-K-0 in 100N oil (5 g/dl) at 70°C.	175
Figure 85. Effect of temperature upon G' of T-34-K-0 in 100N oil (5 g/dl).	176
Figure 86. Effect of temperature upon G'' of T-34-K-0 in 100N oil (5 g/dl).	177
Figure 87. Steady shear viscosity vs. shear rate for D-6.5-ZnAc-100 and D-12-ZnAc-100 in decalin at 5 g/dl and 28°C.	178
Figure 88. Effect of molecular weight on the stress-strain behavior of barium neu- tralized materials.	182
Figure 89. Effect of molecular weight on the stress-strain behavior of zirconium neutralized materials.	184
Figure 90. Effect of cation valence on the stress-strain behavior of materials in molecular weight range of 14500-15000.	185
Figure 91. Effect of molecular weight on the stress relaxation behavior of barium neutralized materials.	187
Figure 92. Effect of molecular weight on the stress relaxation behavior of zirconium neutralized materials.	188
Figure 93. Effect of molecular weight on the creep behavior of barium neutralized materials.	190
Figure 94. Instantaneous set behavior of the materials neutralized with aluminum and zirconium.	191
Figure 95. Stress-strain curves for carboxy-telechelic polyisoprene neutralized with various monovalent and divalent cations.	194
Figure 96. Effect of strain rate on behavior of materials neutralized with Na^+ and K^+	197
Figure 97. Effect of strain rate on behavior of materials neutralized with Mg^{2+} and Ba^{2+}	198
Figure 98. Effect of strain rate on behavior of materials neutralized with Ni^{2+} and Zn^{2+}	199
Figure 99. Stress relaxation and creep curves of carboxy-telechelic polyisoprene neutralized with various cations.	201
Figure 100. Thermomechanical behavior of carboxy-telechelic polyisoprene neu- tralized with various cations.	202

Figure 101. Instantaneous set and hysteresis of carboxy-telechelic polyisoprene neutralized with various cations.	203
Figure 102. Effect of amines on stress-strain behavior of nickel neutralized carboxy-telechelic polyisoprene.	206
Figure 103. Stress-strain behavior of carboxy-telechelic polyisoprene neutralized with various amounts of titanium (IV).	208
Figure 104. Effect of strain rate for materials with Ti/PIP ratios of 1/2 and 1. . . .	211
Figure 105. Effect of strain rate for materials with Ti/PIP ratios of 2 and 3. . . .	212
Figure 106. Stress relaxation and creep behavior of carboxy-telechelic polyisoprene neutralized with various amounts of titanium (IV).	213
Figure 107. Thermomechanical behavior of carboxy-telechelic polyisoprene neutralized with various amounts of titanium (IV).	214
Figure 108. Dynamic mechanical behavior of carboxy-telechelic polyisoprene neutralized with various amounts of titanium (IV).	215
Figure 109. Instantaneous set and hysteresis of carboxy-telechelic polyisoprenes neutralized with various amounts of titanium (IV).	216
Figure 110. Stress-strain behavior of amine-terminated polybutadiene crosslinked with various chlorides.	218
Figure 111. Effect of strain rate on behavior of materials neutralized with CuCl_2 and FeCl_3	219
Figure 112. Stress relaxation and creep behavior of amine-terminated polybutadienes.	220

List of Tables

Table 1. Ultimate Stress and Ultimate Strain of PIP Neutralized with Various Cations 196

Table 2. Ultimate Stress, Ultimate Strain, and Modulus of PIP Neutralized with Various Amounts of Titanium 209

I. Introduction

Polymeric materials have rapidly achieved an enviable position as the class of materials having the highest volume of production, exceeding that of both metals and ceramics. The meteoric rise in the production and utilization of polymers has been due to advances in polymer synthesis which allow the creation of well-defined molecular structures, to new knowledge concerning the relationships between polymer structure and properties, and to an improved understanding of how processing can be used as a tool to develop desirable morphological features. Polymers have truly become “engineered materials” in every sense of the term. As a result of the wide spectrum of desirable properties they may display, polymers are now the material of choice for many diverse engineering applications.

Polymer scientists and engineers are forever seeking to modify the properties of polymers by such techniques as alteration of molecular and morphological structure, reinforcement of a polymeric matrix with a filler or fiber, or blending of existing polymers to create a material which shows properties differing from those of either of the components. The utilization of ionic bonding in polymers has recently attracted widespread interest since it provides an additional means of controlling polymer structure and properties. One class of ion-containing polymers which is currently of great practical and theoretical interest in both the academic and industrial sectors is that of ionomers. An ionomer is a polymer which generally has less than 10-15% ionic groups on an otherwise nonpolar chain. Neutralization of these ionic groups with ions of the

opposite charge results in strong coulombic associations and thus the formation of an ionic network. As would be expected, the ionomer may display properties which are dramatically different from those of the parent polymer. In addition, materials with a broad spectrum of properties may be created by varying the ionic content, neutralizing cation, extent of neutralization, etc.

Although much of the earlier work in the field of ionomers focused on non-elastomeric materials, attention has more recently shifted to elastomeric ionomers due to their commercial potential as thermoplastic elastomers, i.e. elastomers which flow at high temperatures yet retain their network structure at ambient temperatures. For a material to function as a useful elastomer, the polymer molecules must, of course, be connected in some way to one another to prevent flow and permanent deformation when a stress is applied and then released. This has classically been accomplished by covalently crosslinking the chains to form a network. The utility of such a material is obviously limited since it must be crosslinked or cured in the desired end-use shape and cannot be shaped further after the curing process. This shortcoming has been overcome in the block and segmented copolymers since these materials are *physically* instead of *covalently* crosslinked. The components are thermodynamically incompatible and thus phase separate. Since the continuous elastomeric phase is covalently bonded to the glassy or semicrystalline regions, these regions act as physical crosslinks. Above its glass transition and/or melting temperature the hard phase softens to allow flow of the material. The network criterion for elastomeric character may also be satisfied by crosslinking the polymer molecules via strong ionic bonding. Such materials may also serve as thermoplastic elastomers since at higher temperatures the ionic bonds become sufficiently labile to allow flow. Recent work on the solution behavior of ionomers has suggested that they may be useful as fluid additives to modify and control viscosity.

In the conventional ionomers the ionic groups are distributed randomly along the polymer chain. The resulting network structure is thus less than well defined. Another approach is to prepare telechelic ionomers which have the ionic groups located only at the chain ends. This defined chain microstructure leads to a network with much better definition than those resulting from the traditional ionomers in terms of the molecular weight between ionic regions. The task of relating structure to properties is thus somewhat simplified. Such an approach has been taken in the present work. The results of two different joint investigations with other researchers are described. In the first, the bulk and solution properties of sulfonated polyisobutylene telechelic ionomers are reported. These materials were synthesized in the laboratory of Professor Joseph P. Kennedy of The University of Akron. In the second, the results of a study of the bulk mechanical properties of carboxylated elastomeric telechelic ionomers based on polyisoprene and polybutadiene are reported. These materials were synthesized in the laboratory of Professor Robert Jérôme of the University of Liège, Belgium.

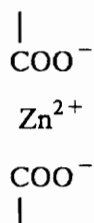
II. Review of Previous Work

This chapter is intended to be an overview of the structure-property behavior of ionomers. The basic chemical structure of ionomers will be considered followed by a discussion of the morphological structure. The discussion of ionomer morphology will include both theoretical and experimental approaches to the problem. It will become clear that this remains a controversial subject even after nearly two decades of research. Thus relating the properties of ionomers to their structure is not always straightforward. The mechanical/viscoelastic behavior of ionomers is then considered. The approach has been to discuss each region of the viscoelastic spectrum separately. This section draws heavily from a recent review by Tant and Wilkes [1] concerning the viscoelastic behavior of ionomers, but has been expanded to include a more thorough discussion of telechelic ionomers - the subject of this dissertation. Other recent reviews on the bulk structure and properties of ionomers have been published by MacKnight and Earnest [2], Banzuin and Eisenberg [3], Longworth [4], and Mauritz and Hopfinger [5]. Finally, the rheological behavior of ionomer solutions is discussed. This is an area in which significant research has occurred only in the last five or so years. Even though it is a relatively new area, a great deal has been learned about the behavior of ionomer solutions. The unusual behavior of ionomer solutions suggests that the future of this area of research holds a great deal of promise.

Structure of Ionomers

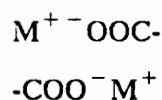
Chemical Structure

Ionomers have traditionally been formed by incorporating acid groups randomly into the polymer chain by copolymerization, or by attaching acid groups randomly along a polymer chain. The typical organic acids such as sulfonic, carboxylic, phosphonic, etc. have generally been used. The idea of neutralizing these acid groups by addition of a cation was first suggested by Brown [6]. The electrostatic attraction between the cations and the acid groups on the polymer chain results in the formation of an ionic network consisting of linear polymer molecules crosslinked by ionic bonding. This association is promoted by the nonpolar nature of the medium which, in turn, is created by the non-polar polymer chain. Brown observed that neutralized carboxylated elastomers behave similarly to vulcanized rubber. This behavior was attributed to the presence of ionic crosslinks such as



in which the zinc ion simply bridges the two carboxylate ions. This simple structure was invoked to describe the behavior of ionomers in much of the early literature, even though it ignores the coordinating tendencies of the cation, the low polarity of the environment resulting from the hydrocarbon backbone, and the presence of polar impurities such as water.

When it was found that neutralization with a monovalent cation produces effects similar to those produced by divalent cations, Otocka, Hellman, and Blyler [7] postulated that dipole-dipole interactions occur between salt pairs, i.e.



Although both of these models have proven to be quite useful in many instances, neither can completely account for the observed behavior of ionomers. The next section on morphological structure will address the question of how the ionic groups interact and what type of structures may be formed.

In addition to using acids as the ionic groups for ionomers, it is also possible to create ionomers using basic groups on the polymer chain and then neutralizing these with an appropriate acid. Hwang, Yang, and Cooper [8] have created polyurethane zwitterionomers which possess both cationic (amine) and anionic (sulfonic acid) groups on the same chain. The basic amine and the sulfonic acid thus neutralize one another. These materials will be discussed in more detail at a later point in this chapter.

Instead of being randomly distributed along the polymer chain, the ionic groups may be located only at the chain ends. This type of telechelic chain microstructure provides a more well-defined molecular weight between ionic groups provided, of course, the molecular weight distribution is relatively narrow. The result is a material with a known molecular weight between ionic crosslinks. Again, the telechelic ionomers will be discussed more fully later in this chapter.

Morphological Structure

The unique properties of ionomers are, of course, a direct result of the interactions between ionic groups. Realizing the importance of understanding the structure of ionomers, Eisenberg [9] first attempted to describe the nature of the ionic interactions and the resulting influence upon morphology. It was assumed that the basic structure present is the contact ion pair in which the cation and anion are separated by their atomic radii. The electrostatic attraction between ion pairs results in the formation of regions consisting only of ionic species. These ionic regions, termed multiplets, specifically exclude the hydrocarbon or nonionic portions of the polymer chains. The size of a multiplet, if a spherical structure is assumed, is thus limited by steric considerations. Eisenberg suggested that the maximum possible multiplet size may be calculated by the equation

$$r_m = \frac{3v_p}{S_{ch}} \quad (2.1)$$

where r_m is the multiplet radius, v_p is the volume of an ion pair, and S_{ch} is the area of the hydrocarbon chain in contact with the spherical surface of the multiplet. For an ethylene - sodium methacrylate copolymer this results in a multiplet radius of about 3 Å , which corresponds to a volume containing eight ion pairs. Thus multiplets of spherical geometry must be quite small. Should multiplets exist as lamellar structures, however, there is essentially no limit to the maximum size allowed by steric considerations.

Eisenberg suggested that multiplets may further associate to form larger structures called clusters. These clusters consist of a group of multiplets ranging in size from a

single ion pair to the maximum size allowed by steric restrictions. The multiplets which make up the cluster are separated by a hydrocarbon skin consisting of the nonionic portions of the chains. The maximum cluster size is limited by the elasticity of the polymer molecules.

It is clear that the optimum cluster size depends upon a balance between the electrostatic and elastic forces. The electrostatic interactions are calculated assuming that energy is released during cluster formation with the work being dependent upon both the geometry of the cluster as well as the dielectric constant of the medium. The elastic forces are calculated to a first approximation using the Gaussian theory of rubber elasticity. The electrostatic forces are weakly dependent upon temperature while the elastic forces are proportional to temperature. Thus there is a critical temperature at which clusters become unstable. It is also clear that for low ion concentrations the elastic forces would tend to be greater than at higher ion concentrations. This suggests that there may be a critical ion concentration for cluster formation. We shall see later that viscoelastic properties as well as other experimental results support the possibility of such a morphological transition for some ionomers.

X-ray scattering experiments have shown that neutralized ionomers often display a small angle scattering peak while the same ionomers which have not been neutralized may not. Figure 1 shows such an "ionic peak" for the sodium salt of an ethylene - methacrylic acid copolymer along with the scattering curves for the acid form of the copolymer and low density polyethylene [10]. The fact that the ionic peak is observed only for the neutralized ionomer suggests that a change in structure occurs upon neutralization or that the electron density difference becomes sufficient for detection. Both the magnitude and location of the ionic peak depend upon the cation, and the peak is destroyed when the ionomer is saturated with water. The ionic peak has been the basis of structural models proposed by several groups of investigators.

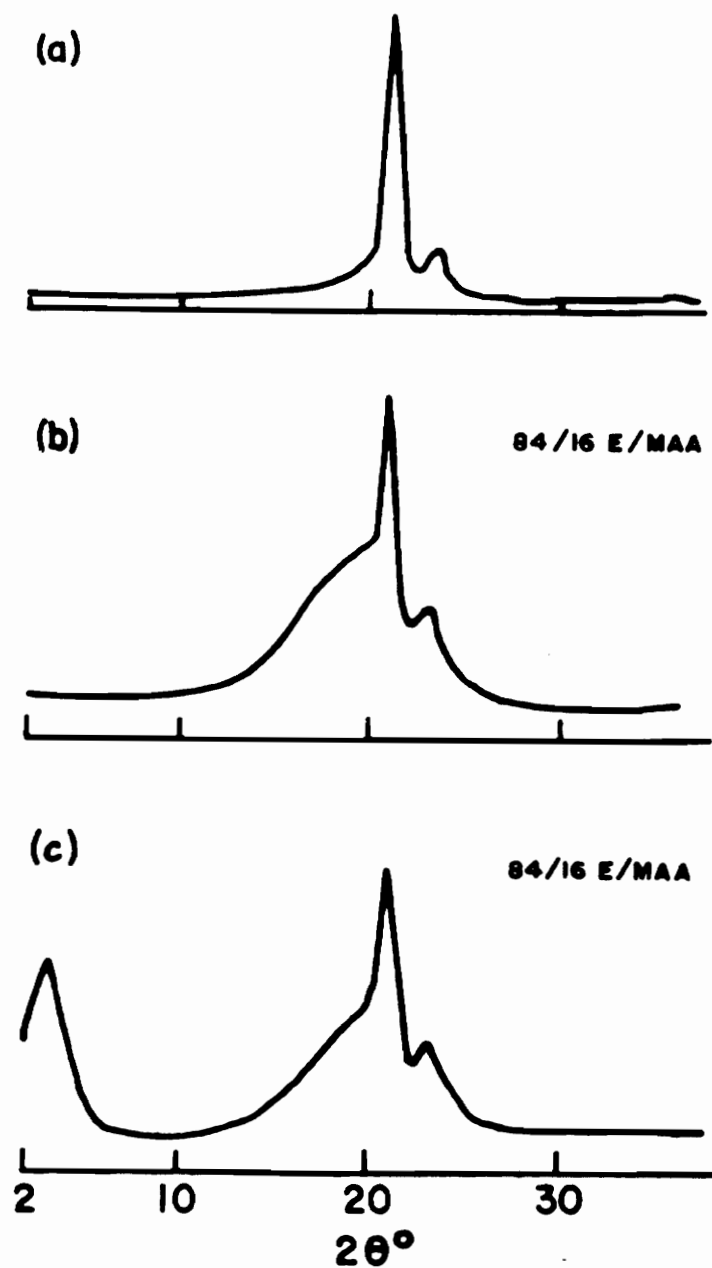


Figure 1. X-ray scattering curves of polyethylene-based materials: (a) low density polyethylene, (b) ethylene - methacrylic acid copolymer (5.8 mole % acid), and (c) the 100% neutralized sodium salt of (b). From Longworth [10].

Longworth and Vaughan [11] assumed that the ionic peak is a Bragg diffraction maximum, and suggested that there is a repeat unit of regions of ordered hydrocarbon chains with a repeat distance of about 20 Å (determined from the scattering angle). These regions of ordered hydrocarbon segments were said to arise due to the clustering of coordinated metal ions. The problems with this model, according to MacKnight and Earnest [2], are that: (1) it is difficult to envision a potential capable of producing such a regular distance between multiplets when the multiplets occur randomly along the polymer chains, and (2) the model does not adequately account for the intensity differences in the ionic peak for different cations.

Marx, Caulfield, and Cooper [12] proposed a model which assumes that no phase separation occurs, the acid groups existing as aggregates homogeneously distributed in the amorphous phase. These aggregates consist of two or more acid groups and contain both protons and the metal cations. It was postulated that the ionic peak arises due to the difference in electron density between the cations and the hydrocarbon, the cations being considered point scatterers distributed on a paracrystalline lattice. MacKnight and Earnest [2] point out that it is not clear what is the origin of the potential which must impose the regularity required for such a structure in an amorphous, random copolymer. These authors also point out that the model does not explain why the ionic peak is not present in the acid form but is present when neutralized with lithium (a poor scatterer of x-rays) when there is very little difference in the electron density between lithium carboxylate and the carboxylic acid. (Sulfonate ionomers may even show a peak in the unneutralized form, as has been shown by Weiss and Lefelar [57].) Binsbergen and Kroon [13] proposed a very similar aggregate model which has the same shortcomings as that of Marx et al.

MacKnight, Taggart, and Stein [14] developed a model based upon a radial distribution function (RDF) analysis and an analysis of small-angle x-ray scattering using the

theories of Porod [15] and Guinier and Fornet [16]. The materials studied were ethylene based ionomers of acrylic and methacrylic acid ranging in acid concentration from 2 to 7 mole percent. The details of this study are much too lengthy to be presented here and thus we will move directly to the very important results obtained. The RDF analysis suggests that the ionic peak does not arise from interference between scattering centers since the distance between the clusters would have to be several hundred angstroms. The results of the small-angle x-ray scattering suggest that there are ionic clusters of 8-10 Å in radius randomly distributed in the amorphous hydrocarbon matrix. The proposed model assumes that the fundamental structure is the coordinated metal ion and that there is a tendency toward a charge imbalance within the cluster. Matrix ions surrounding the cluster are attracted to it but cannot approach more closely than allowed by the hydrocarbon shell surrounding the cluster, so that there is an outer shell of ions with a lower charge density than the core. These two opposing mechanisms thus establish a preferred distance of 20 Å between the cluster and matrix ions, and this is the proposed origin of the ionic peak. These workers also suggest that when the material is saturated with water the water molecules tend to congregate near the cluster. They may coordinate with the matrix ions and their presence will raise the local dielectric constant. Thus the preferred distance and the ionic peak are destroyed but the cluster is left intact. A schematic of the model is shown in Figure 2. That the model can explain the disappearance of the ionic peak in the presence of water is certainly significant.

Pineri and coworkers [17-20] have used, in addition to x-ray scattering, the techniques of electron microscopy, electron spin resonance (esr), Mossbauer spectroscopy, and small-angle neutron scattering (SANS). Meyer and Pineri [20] studied Fe(II) complexes of a butadiene-styrene-vinylpyridine terpolymer (85% butadiene, 10% styrene, and 5% vinylpyridine). Utilizing neutron and x-ray scattering these workers determined that more than 82% of the clusters are less than 30 Å in radius and that the average

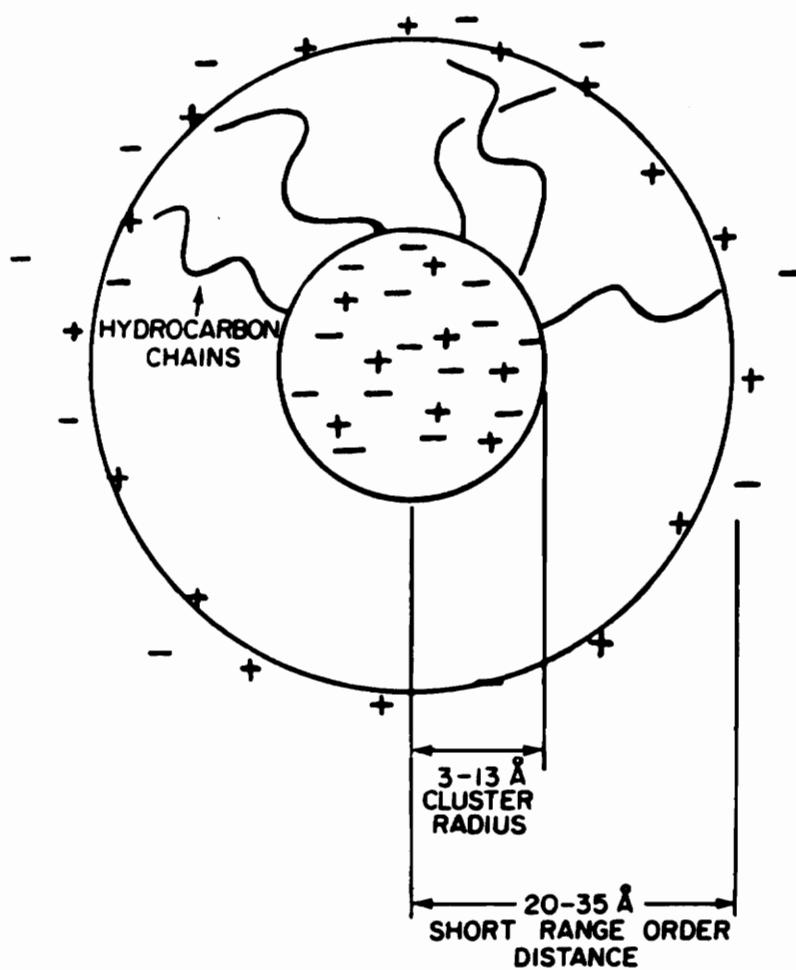


Figure 2. Schematic of MacKnight, Taggart, and Stein model: From [14].

cluster radius is about 10 Å , in good agreement with the results of MacKnight, Taggart, and Stein [14]. They also determined that there are three different types of ionic aggregates present, with two of them being essentially the shell-core structure proposed by MacKnight, Taggart, and Stein.

Fujimura, Hashimoto, and Kawai [21] suggested a slight variation of the core-shell model of MacKnight, Taggart, and Stein. In this model, the electron density profile is modified somewhat. The hydrocarbon shell is considered to be depleted of ions while the matrix has a finite ion concentration. This model is illustrated in Figure 3.

Yarusso and Cooper [22] have taken the approach of using the previously proposed models and calculating the scattering curves which would result from each. They were unable to fit the actual scattering data of a series of zinc-neutralized sulfonated polystyrenes using any of the models. They thus proposed a modified hard-sphere model similar to that of MacKnight et al. [14]. It was assumed that the hydrocarbon shell surrounding the core provides a barrier for the closest approach of the ionic aggregates. The electron density of the hydrocarbon shell is the same as that for the matrix, and there is no secondary ionic shell. The ionic aggregates are arranged with a liquid-like degree of order. This model is illustrated in Figure 4. Yarusso and Cooper were able to fit the scattering curves of the zinc sulfonate polystyrenes except in the region of very low angles. In further work, they utilized the model to fit SAXS curves of other types of ionomers [23].

The theoreticians have also joined in the effort to describe exactly how ion aggregation occurs. Forsman [24,25] has used a statistical mechanical approach to develop a model in which nearest neighbors interact to form an aggregate about a central site. Dreyfus [26,27] has more recently developed a model in which a cluster is built up from the center by closest packing, thus resulting in a charge distribution which decreases monotonically from the center. Because of their complexity, the details of the develop-

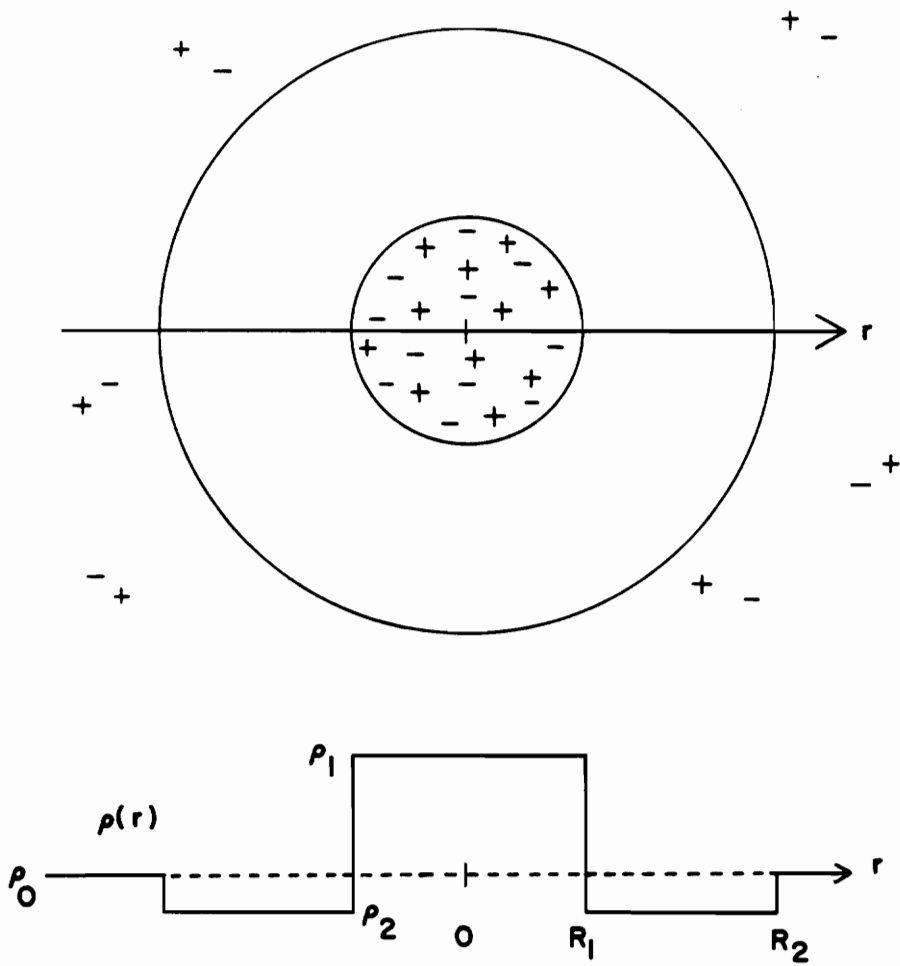


Figure 3. Schematic of Fujimura, Hashimoto, and Kawai model: From [21].

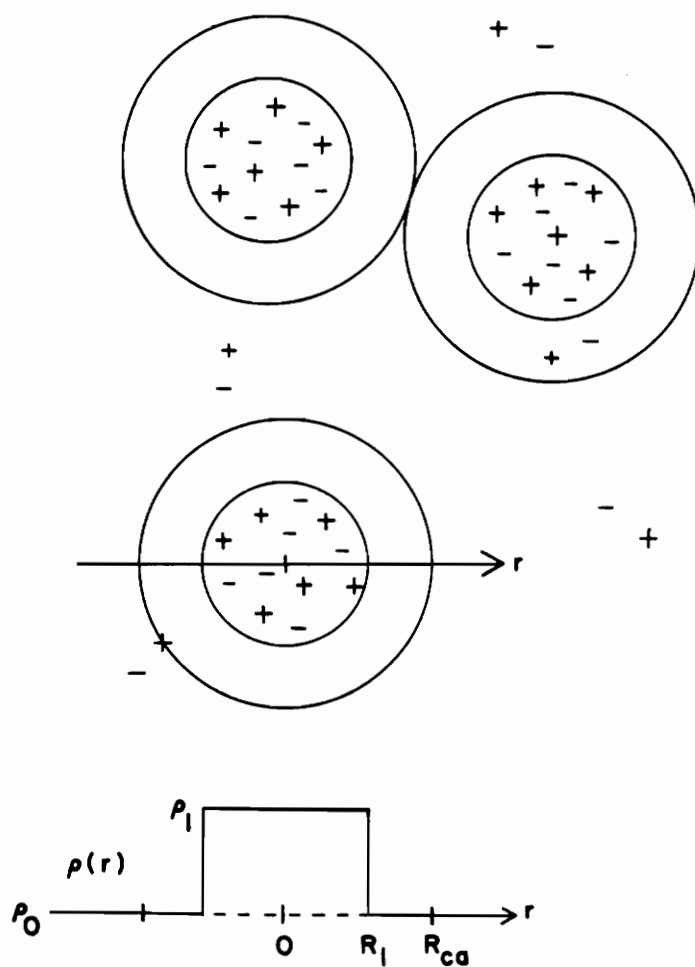


Figure 4. Schematic of Yarusso and Cooper model: From [22].

ment of these models will not be discussed here. It is, however, important to point out that there remains a great deal of controversy concerning the structure of ionic aggregates in ionomers. In addition to utilizing SAXS to probe the structure of these aggregates, experimentalists have utilized infrared spectroscopy [28-32], Raman spectroscopy [33-35], extended x-ray absorption fine structure (EXAFS) [36-38], electron spin resonance [17,18,20,39], and electron microscopy [40]. Even with this battery of experimental techniques directed at the problem, the elucidation of ionomer morphology remains an elusive goal.

Mechanical/Viscoelastic Behavior of Ionomers

In this section the mechanical and viscoelastic behavior of bulk ionomers is considered. As mentioned earlier, each of the four major regions of the viscoelastic spectrum will be considered separately. It will become apparent that the relationship between the average ionic relaxation time and the relaxation time spectrum of the base polymer strongly affects the response of the system in each of the four regions. This, in turn, strongly influences the potential applications of ionomers as well as their processability. For example, if the glass transition temperature of the polymer is exceeded but if the ionic associations remain strong at the desired processing temperature, then processability may be hindered or rendered impossible. Thus, it is important to select the type of ionic groups which will deliver the desired properties at the use temperature and also allow flow and processing at the desired temperature.

Behavior in the Glassy Region

With respect to the viscoelastic response of a system in the glassy state, the presence of ionic groups has not resulted in major changes in properties although the dynamic mechanical behavior is somewhat altered. As an example, Drzewinski and MacKnight [41] noted that as the level of sulfonation of polysulfone increased, the low temperature loss behavior was changed. In fact, it was suggested that the sulfonated portion of the chain gives rise to a new loss peak. As might be expected, the moisture content was found to influence the sub- T_g loss character, although no major molecular explanation for this effect was offered. Nakano and MacKnight [42] have observed that incorporating ionic species within the backbone has diminished or somewhat shifted the previous sub- T_g loss behavior of the ion-free backbone. This observation has been accounted for on the basis of more restriction of localized molecular motion which is the basis of sub- T_g relaxations.

Little data appears to exist concerning the effect of ionic species on the glassy state properties such as the more common viscoelastic or mechanical properties of impact, stress-strain characteristics, etc. However, the author is aware of some studies yet to be reported [43] which indicate that ionomer glasses may have increased mechanical fatigue resistance relative to the un-ionized polymer. This suggests that crazing and/or shear yield behavior may also be altered by the presence of ionic species, but no data has been located to either confirm or disprove this speculation. It would appear that additional studies in the area of glassy ionomers may be fruitful in terms of leading to an enhancement of the mechanical properties and, at the same time, provide another route to obtaining a better understanding of the structure-property behavior of ionomers in general.

There is a great deal of data which confirms that the glass transition temperature is influenced by the presence of ions. It has been established through the studies of Matsuura and Eisenberg [44] and Eisenberg, Matsuura, and Yokoyama [45] that ionic associations may considerably raise T_g due to the restriction of backbone motion - the origin of T_g . However, the nature of this T_g enhancement is dependent upon whether the ionic species exist within the backbone in a random manner or at the terminal points of the molecule (telechelic systems). In the case of the random copolymer ionomers, the association of the ionized species clearly can place limitations on backbone mobility through the “ionic crosslinks”. Thus a higher thermal energy is required to induce the same backbone mobility and this results in an increase in T_g . In fact, the degree to which mobility is restricted due to ionic interactions can often be correlated to the q/a ratio and its product with the concentration, c , of the ionic species for Groups I and II of the periodic table [44,45]. Specifically, Matsuura and Eisenberg have nicely demonstrated that the enhancement of T_g of many random copolymer ionomers can be “normalized” when plotted against this product as shown in Figure 5.

As has been pointed out by Jérôme et al. [46], the influence of ions on the backbone transition may also be a function of the measurement or observation time (scan rate), the relative backbone chemistry (stiff or flexible), and the strength of ion association at the test temperature. Specifically, in those systems in which the backbone is flexible and the T_g is therefore low, strong association of ionic groups may place restrictions on backbone mobility and thus raise T_g . However, the same ionic groups in a high glass transition or stiff backbone polymer may well have reached a much weaker association due to the greater thermal energy present when the glass transition temperature of the backbone is approached. The ions might thus have little or no effect on T_g in this case. In fact, in the work of Besso et al. [47] on carboxylated-phenylated polyphenylene which possesses a high glass transition temperature (ca. 290°C), it was found that there was

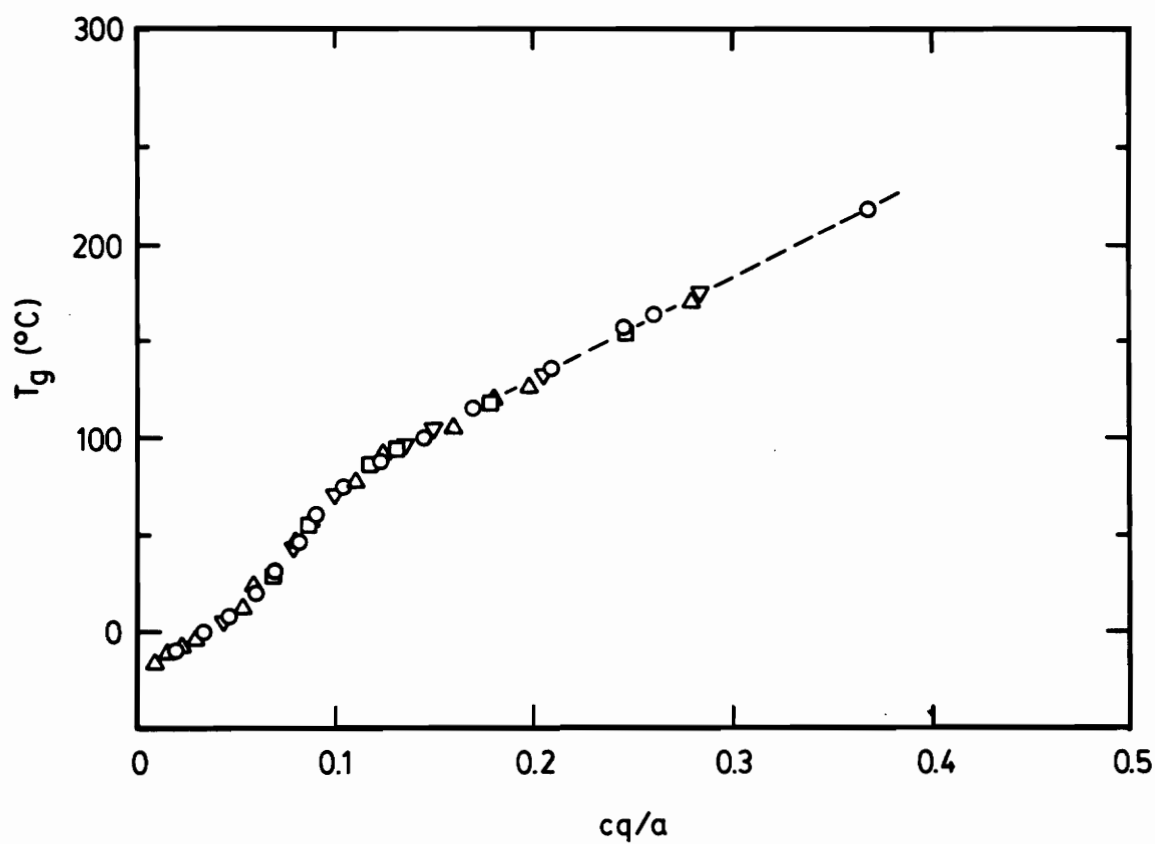


Figure 5. Plot of glass transition temperature vs. cq/a : Data is for ethyl acrylate - acrylic acid copolymers neutralized with various cations. From Matsuura and Eisenberg [44].

a less pronounced effect of ionic groups on the glass transition temperature than had been observed for similar ionic contents in more flexible backbone systems.

As might be expected, moisture or other small highly polar liquid species can be preferentially sorbed into the multiplet regions thereby leading to plasticization effects. Such additives are ionic plasticizers as opposed to the more typical nonionic plasticizers. Whether such plasticization results in a shift in T_g (and thus alters viscoelastic behavior) will depend upon the level of sorption, concentration of ionic species, and backbone stiffness. It is obvious that there is also the possibility for such species to be lost during a thermal scan if the T_g is in the region where the plasticizer is volatile.

In summary, ionic moieties may often raise the glass transition temperature and thereby alter the viscoelastic response of a material if these ionic associations have a sufficiently long relaxation time relative to the backbone relaxation times associated with the glass transition temperature. If, however, the ionic associations are of a much shorter time scale than the backbone motions, such influence may be diminished to zero.

Behavior in the Glass Transition Region

One of the most extensively studied parts of the viscoelastic spectrum is the glass transition region which bridges at higher temperatures to the rubbery plateau region. From a practical point of view, it is clear that since the properties on either side of the transition region are so different, it is necessary to understand the variables which influence when or where this transition will occur, i.e. changes in temperature, deformation rate, plasticizer content, etc.

The use of the well-known WLF relationship has been quite successful in predicting the behavior in the transition region by interrelating the two important external variables of time and temperature along with the T_g and the two constants well known as

C_1 and C_2 . In particular the WLF relationship generally is used to predict changes in properties over the range of T_g to $T_g + 100^\circ\text{C}$, although its applicability has been observed somewhat beyond these limits. At higher temperatures, an Arrhenius single activation energy parameter may be sufficient to allow the prediction of changes in many viscoelastic properties. The data required for testing or utilizing the WLF equation (or the Arrhenius equation) can be obtained by a number of methods. These may be dynamic or may be static measurements of more transient phenomena such as would occur in stress relaxation or creep experiments [48-52]. While the majority of such testing procedures have relied on relatively low strain properties for past studies on ionomers, it should be pointed out that higher deformation and even ultimate properties such as tensile strength have been correlated to time-temperature considerations as has been discussed by Smith and Chu [53]. To the author's knowledge, no such attempts have been made utilizing similar treatments for the case of ionomer systems, but it certainly would be of interest to attempt such an approach.

The WLF equation is derived from concepts associated with thermally induced changes in free volume, and relates the time domain to temperature. Increasing temperature increases both free volume and Brownian motion. Hence, increasing the temperature, which speeds up molecular motion, is like watching the system at longer times at the original temperature. That is, the experimental time frame can be shortened by an increase in temperature for the purpose of observing the same viscoelastic response in a shorter time period. Qualitatively, this same concept can be expressed in terms of the Deborah number, N_{Dn} , which is a dimensionless ratio of the molecular response time to the experimental time frame. If this number is greater than unity the system appears more solid-like, whereas when it decreases below unity the system transforms to what appears to the observer as a liquid.

While the Deborah number is a more general concept, the WLF equation, which is often the basis for quantitative interpretation of viscoelastic data, has limits to its utility. If there is a change in molecular mechanism(s) controlling the response time of a system, e.g. crosslinking, crystallization, break-up of multiplets or clusters, etc., then time-temperature superposition will be limited in its applicability. Indeed, it has been the observation of deviation from WLF behavior or time-temperature superposition that has been one of the foremost causes for argument concerning the presence of clustered morphologies in ionomer systems [54-56]. Specifically, it is a very general observation that the WLF or master curve approach can be utilized in ionomers up to a critical ion concentration, but above this concentration time-temperature superposition will no longer hold. This is illustrated in Figure 6, which shows some stress relaxation master curves and so-called pseudomaster curves for six sodium-neutralized poly(ethyl acrylate) ionomers obtained by Eisenberg et al. [50]. It is observed that at low ionic content, while the transition region is broadened over the time spectrum at a given temperature due to ionic association, the WLF relationship or general time-temperature superposition principle will describe the data quite well. However, the values of the constants C_1 and C_2 are not necessarily the universal values normally found when T_g is the reference temperature. Above a critical ion concentration, however, shifting of the stress relaxation curves to form a master curve clearly fails due to the deviation from a single master curve. While a single master curve will describe the data at lower mole percentages, it is clear that its breadth is increased and, for the stress relaxation data shown, higher ionic contents result in less relaxation within the same time frame. This, of course, is no surprise since flow is more limited by the ionic species.

The transition from a simple master curve to what Eisenberg et al. [50] refer to as a pseudomaster curve where time-temperature superposition no longer holds suggests that a change in relaxation mechanism is involved. A change in relaxation mechanism

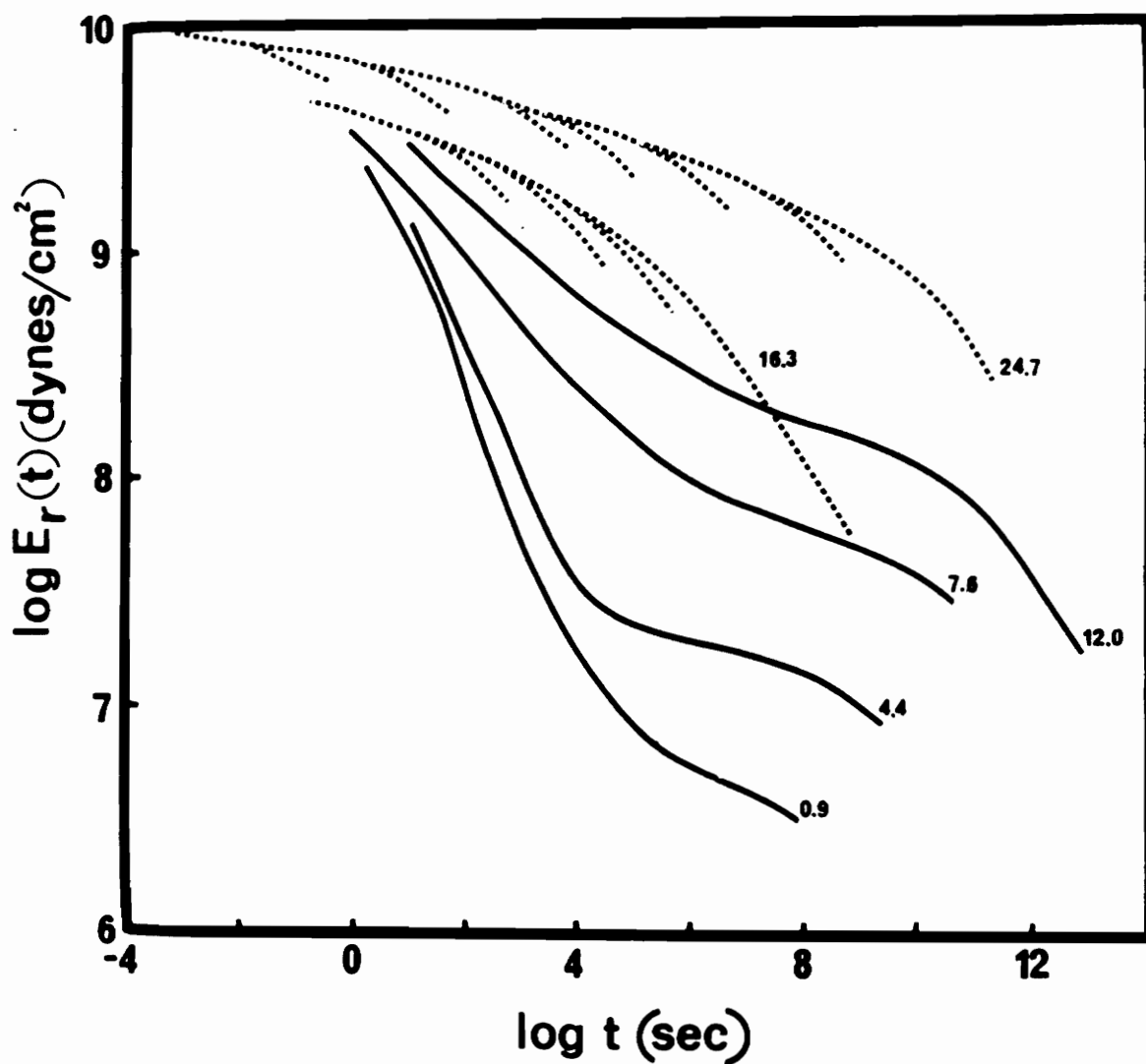


Figure 6. Stress relaxation master and pseudomaster curves for six ionomers: Poly(ethyl acrylate) ionomers neutralized with sodium. The numbers indicate ion concentrations (mole %). From Eisenberg et al. [50].

may be the result of a structural change. In the case of ionomers, it has been this type of viscoelastic analysis which has suggested that, at a sufficiently high concentration of ions, the multiplets induced at lower concentration begin to cluster and a higher population of this latter morphology develops. It is this cluster structure and its different relaxation behavior which is believed to cause deviation from time-temperature superposition. What is not clear, however, are the details of what actual molecular mechanisms are responsible for the change in relaxation characteristics caused by the cluster morphology, i.e. the potential loosening or “dissolution” of clusters caused by the higher thermal energy. The idea of cluster break-up, however, must be questioned. For example, through SAXS experiments it has been demonstrated that in some systems the so-called ionic peak can exist to extremely high temperatures as has been discussed by Longworth [10], Yarusso and Cooper [23], and Weiss and Lefelar [57]. Indeed, if ionic species are present in a low dielectric medium, it is not surprising that a phase separation of the ionic species may persist even though their strength of association may be extremely weakened at higher temperatures. Hence, they may readily break up when deformed, such as in melt processing, and have little influence on the processing window if at a sufficiently high temperature. Certainly the persistence of strongly binding clusters and multiplets at a given temperature will be highly dependent on the nature of the anion and cation species as has been discussed earlier, e.g. the carboxylates are less strongly associated than sulfonates, other factors being equal [58].

Concerning the Arrhenius approach for time-temperature superposition, i.e. a reciprocal temperature dependence, this has indeed been found to apply in some cases. But often the data utilized to reach this conclusion is obtained over a limited temperature range, and it is well known that over a narrow temperature range an activation energy plot may well be linear even though the process may not really obey an Arrhenius temperature dependence over a broader range of temperatures. Thus “over-

interpretation" of results may lead to poor predictions outside of the temperature range of available data.

Time-temperature superposition approaches have been utilized to look at the viscoelastic response of other types of ionic systems. One example that might be mentioned is by Granick [59] who noted that the stress relaxation modulus curves for sulfonated EPDM's containing the ionic plasticizer zinc stearate did not superpose. Indeed, it is of no surprise that deviations from the master curve occurred due to the fact that there is a broad distribution of melting characteristics of the zinc stearate located in the ionic regions [60]. Due to this melting distribution and hence temperature dependent plasticization by the liquid zinc stearate after melting, this structural change would certainly alter relaxation characteristics as was observed. Similar changes in viscoelastic behavior with loss of water or other types of volatile ionic species would also be expected. Another case in which time-temperature superposition would be limited is when either crystallization or melting of the nonionic backbone may occur with time such as in the methacrylic acid copolymers.

Time-temperature superposition principles have also been applied to the telechelic systems in addition to the random type already discussed. In these ionomers having a more well-defined chain structure, it is again found that time-temperature superposition holds well particularly when the molecular weight of the telechelic species is high enough so that the concentration of terminal ionic species is low enough to minimize cluster formation. However, in the case of lower molecular weight telechelics where a low polarity backbone exists, as in polyisoprene, polybutadiene, and polyisobutylene, clusters have been proposed to exist although there are some interesting possible variations on what the term cluster may mean. Systematic SAXS studies of telechelic ionomers of known molecular weight have led to the suggestion that a layer-like or lamellar form of ionic domains may exist in contrast to the more spherical type proposed for random

ionomers [61-63]. There has even been some hint of such lamellar structures in the random systems, but the data supporting this hypothesis has been rather limited. Such postulations must be taken with caution, although they may well be correct for specific systems.

It is clear that the viscoelastic properties in the glass transition region may be highly influenced by the presence of multiplets and higher order structures such as clusters. The molecular interpretation of their influence and the effect of the dielectric constant of the medium, strength of ionic association as controlled by steric hindrance, choice of neutralizing ion species, presence of plasticizer, presence of excess neutralizing agent, etc. still require much further research.

While the general nature of ionic associations and their effect is obvious, no general approach is likely to ensure the predictability of viscoelastic behavior for all ionic systems in the transition region. This is a result of the number of important variables that can change in terms of system preparation as well as possible alteration of morphology as a result of thermal cycling [64]. This implies that the development of an equilibrium structure may be dependent upon time as well as temperature. Hence, the methods used to prepare films, melt samples, and solutions may lead to specific results that are partially dependent upon the method of preparation. This statement is strongly supported by the work of Lundberg and Phillips [65] concerning ionomer solutions and the dependence of their viscoelastic response upon the method of preparation.

Behavior in the Rubbery Region

The rubbery region of the viscoelastic spectrum of ionomers is currently of great importance due to the interest in utilizing ionic interactions to create thermoplastic elastomers. The rubbery state, of course, occurs above the glass transition temperature

and is characterized by a plateau modulus in the vicinity of 0.1-0.2 MPa. In this region of viscoelastic behavior the macromolecular backbones possess sufficient energy to be quite mobile, but are restricted from actually flowing by either chemical or physical crosslinks which connect the chains. When an elastomer is released following a deformation, these crosslinks, along with the entropic elasticity of the chains, provide sufficient memory of the initial undeformed state to return the material to or close to this state. Classically, elastomers such as natural rubber, polybutadiene, polyisoprene, etc. have been crosslinked via permanent covalent bonding. These materials, once crosslinked, cannot flow at any temperature and their shaping operations are thus quite limited. The advent of the thermoplastic elastomeric block and segmented copolymers extended the usability and versatility of elastomers since these materials flow sufficiently well in the melt state to allow processing by injection molding. The physical crosslinking of these materials occurs, of course, due to the glassy or semicrystalline regions which are dispersed in an elastomeric matrix, the different components of each phase being covalently bonded to one another. Ionic bonding provides another way to physically crosslink elastomers, since at higher temperatures these ionic bonds may become weakened enough to allow melt flow and processing.

Although our discussions to this point have principally concerned the viscoelastic behavior of ionomers derived from glassy polymers, the first ionomers were actually based on elastomers. Carboxylic acid groups were initially introduced into the polymer chain as a means of controlling polarity. The first such commercial product was a butadiene-styrene-acrylic acid terpolymer latex (trade name Hycar 1571) marketed by B. F. Goodrich in 1949 [66]. It was Brown who first neutralized carboxylated elastomers with metal oxides in the early 1950's thus actually forming ionically crosslinked elastomers [67]. His work catalyzed the development of an entire new class of polymeric materials. In 1957 and 1963 he published reviews describing the carboxylated elastomers

[66,68]. A more recent review of carboxylated elastomers was presented by Jenkins and Duck [69].

Following the pioneering work of Brown, a shift in emphasis to non-elastomeric ionomers was probably a result of the poor mechanical properties of carboxylated elastomers. However, sulfonated ionomers have since been found to have much better mechanical properties than the carboxylated ionomers. As mentioned earlier, Lundberg and Makowski [58] demonstrated very clearly that sulfonated polystyrene shows much stronger ionic bonding than the corresponding carboxylated materials. With the advent of the sulfonated ionomers, new interest in the ion-containing elastomers was generated. Esso patents in the mid-seventies [70-72] on sulfonated EPDM materials revitalized the efforts to probe the potential of elastomeric ionomers. However, it was not until 1978 that the first data on EPDM based ionomers were published in the open literature. Since then there has been a substantial increase in research efforts aimed at developing an understanding of these and other elastomeric ionomers.

Sulfonated EPDM.

The EPDM systems are terpolymers of ethylene, propylene, and a non-conjugated diene monomer (e.g. ethylidene norbornene or ENB) which are polymerized by a Ziegler-Natta or coordination mechanism. Details of the synthesis, sulfonation, and neutralization procedures have been presented by Makowski et al. [73]. Agarwal, Makowski, and Lundberg [48] have studied the viscoelastic behavior of the bulk material as a function of both sulfonate content and neutralizing cation. Figure 7 shows the effect of sulfonate content on the storage modulus as a function of temperature. The base EPDM polymer shows only a short pseudo-rubbery plateau near room temperature indicating the presence of entanglements but no crosslinking. However, upon light

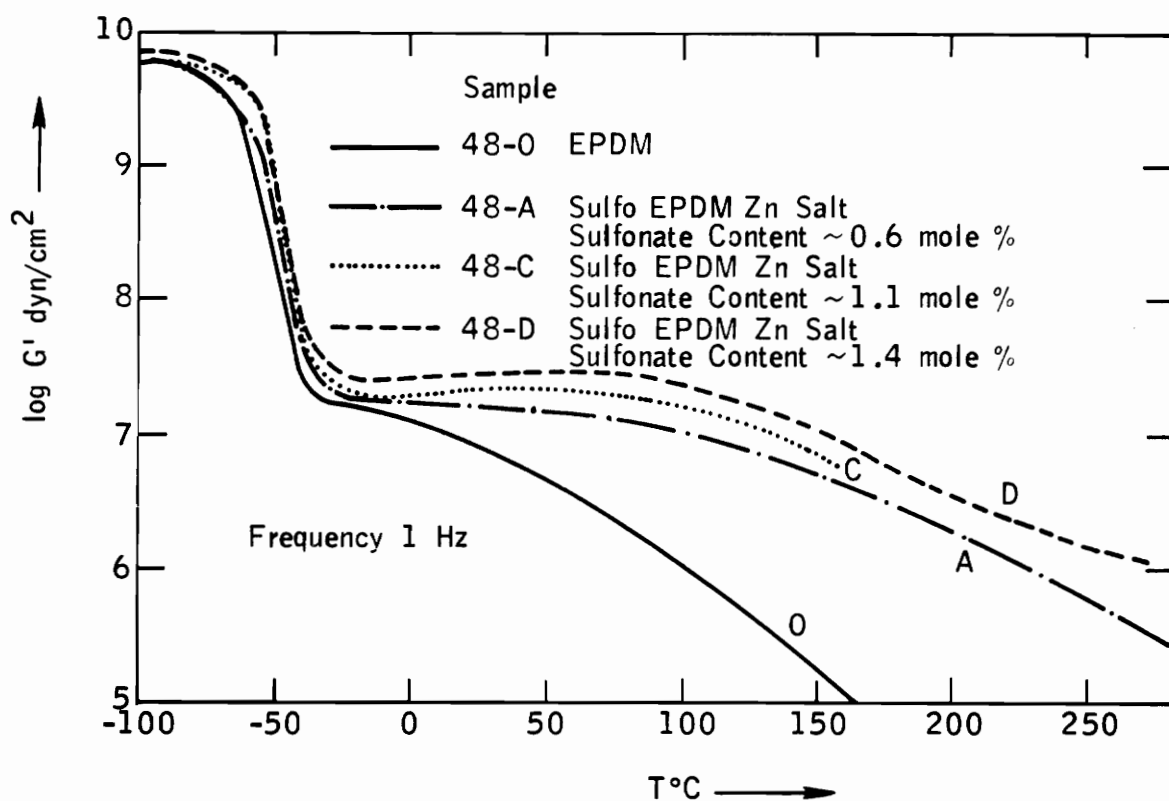


Figure 7. Storage modulus G' vs. temperature for zinc sulfonate EPDM's: Levels of sulfonate content are indicated. From Agarwal et al. [48].

sulfonation (0.6 mole percent) and neutralization, a well-defined rubbery plateau is observed. The materials with sulfonate content of 1.1 and 1.4 mole percent actually show a slight increase in G' with increasing temperature which are in accordance with rubber elasticity theory. At higher temperatures the ionic aggregates weaken and the materials are observed to flow. The level of sulfonation was quite low, 0.6 to 1.4 mole percent, and was found to have no significant effect on T_g . The time-temperature superposition principle was found to be valid for all of these ionomers. These observations support a non-clustered or multiplet morphology in these EPDM sulfonate ionomers.

The type of cation used for neutralization was found to have a much smaller effect on the viscoelastic properties. The cations studied include Li^+ , Cs^+ , NH_4^+ , Mg^{2+} , Ba^{2+} , Zn^{2+} , and Pb^{2+} . The primary observations were that Ba^{2+} resulted in a higher G' (and thus a tighter network) than any of the other cations at the same frequency. The NH_4^+ material displayed a decreasing G' at lower temperatures than the others (likely due to its bulkiness) as did Zn^{2+} (likely due to its greater covalent character). The type of cation also had no significant influence on the T_g at least at these low mole percentages.

The effect of different cations on the tensile and melt flow behavior of these ionomers was also investigated by Makowski and Lundberg [74]. The cations studied were Li^+ , Na^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Co^{2+} , and Zn^{2+} . Zinc-neutralized ionomers displayed the highest melt index (0.75 at 190°C, 478 psi) followed by lead (0.1), while the other materials did not flow at all (melt index of 0). The tensile properties of zinc-neutralized ionomers were found to be equal to or greater than those for the other materials. This combination of good mechanical properties and low melt viscosity at elevated temperatures indicates that the zinc-neutralized ionomers are potentially the most suitable from a melt processing point of view.

These workers also found that the melt viscosity of zinc-neutralized EPDM sulfonate ionomers can be further reduced by use of an ionic plasticizer such as zinc stearate. The zinc stearate interacts strongly with the sulfonate groups at elevated temperatures, thereby tending to break up the ionic associations and reduce the viscosity. Upon cooling to ambient temperatures the zinc stearate separates out via crystallization and acts as a reinforcing filler to enhance the modulus. These effects can be clearly seen in the viscoelastic behavior. In the plateau region extending from T_g to about 100°C, G' increases with increasing zinc stearate content (up to 19.0 g $\text{Zn}(\text{St})_2/100$ g polymer) due to a "filler" effect. Upon reaching the T_m of zinc stearate, the non-crystalline zinc stearate solvates the ionic groups and G' is observed to decrease in the melt flow region with increasing zinc stearate content. Thus, through a suitable choice of molecular weight, sulfonate content, neutralizing cation, and ionic plasticizer, it is possible to obtain metal sulfonate EPDM's with good mechanical properties and sufficiently low melt viscosity for processing.

Carboxylated Elastomeric Telechelic Ionomers.

For the elastomeric materials discussed to this point, the ionic groups have been distributed in a random fashion along the polymer chain. Neutralization of these ionic groups then results in a rather ill-defined network in which the molecular weight between ionic crosslinks may vary greatly. Also, the presence of dangling or free chain ends will influence the viscoelastic behavior in the rubbery region. A more recently developed approach to give better definition to the location of ionizable species is the telechelic class of ionomers. This approach was first pursued by Ostocka, Hellman, and Blyler [7], who studied the bulk and solution viscosity of carboxy-terminated polybutadiene in both the unneutralized and neutralized forms. Extensive research on carboxylated elastomeric

telechelic ionomers has been conducted by Otocka et al. [7], Pineri et al. [17], and more recently by Broze, Jérôme, Teyssié, and coworkers [46,63,75-80].

The work of Broze et al. has been focused on linear carboxylated telechelic ionomers based on polybutadiene and polyisoprene. The carboxy-terminated polybutadiene was obtained commercially and had an \overline{M}_n of 4600 and of dispersity ratio of 1.8. The carboxy-terminated polyisoprene was prepared with a variety of molecular weights and a dispersity ratio of less than 1.2. Figure 8 shows the viscoelastic behavior of both the carboxy-telechelic polybutadiene and the same material neutralized with magnesium. It is clear that the material is transformed from a rather viscous fluid to a material which displays a low-frequency flow region as well as a high-frequency plateau region corresponding to a network-like response. While the time-temperature superposition principle is found to be valid in this case, the shift factor, a_T does not obey a WLF type of temperature dependence. However, linear behavior results when $\log a_T$ is plotted vs. $1/T$. Therefore, an Arrhenius type of temperature dependence is observed. Materials neutralized with calcium and zinc display qualitatively similar viscoelastic behavior. The values of G' and G'' for the zinc material cross at a much higher frequency due to the greater covalent character of the zinc bond which results in a weaker network and more flow. The materials neutralized with barium and beryllium exhibit network-like behavior over a much wider range of frequency and temperature, but according to the authors, for fundamentally different reasons. The Be carboxylates form small and very tight multiplets due to high electrostatic interactions, while the Ba carboxylates were postulated to favor a larger extension of the two-dimensional growth of multiplets into layered structures.

The ability to control the molecular weight of the carboxy-telechelic polyisoprene has given these workers the opportunity to study the effects of molecular weight on the viscoelastic behavior [77,80]. Obviously, for telechelic ionomers the molecular weight

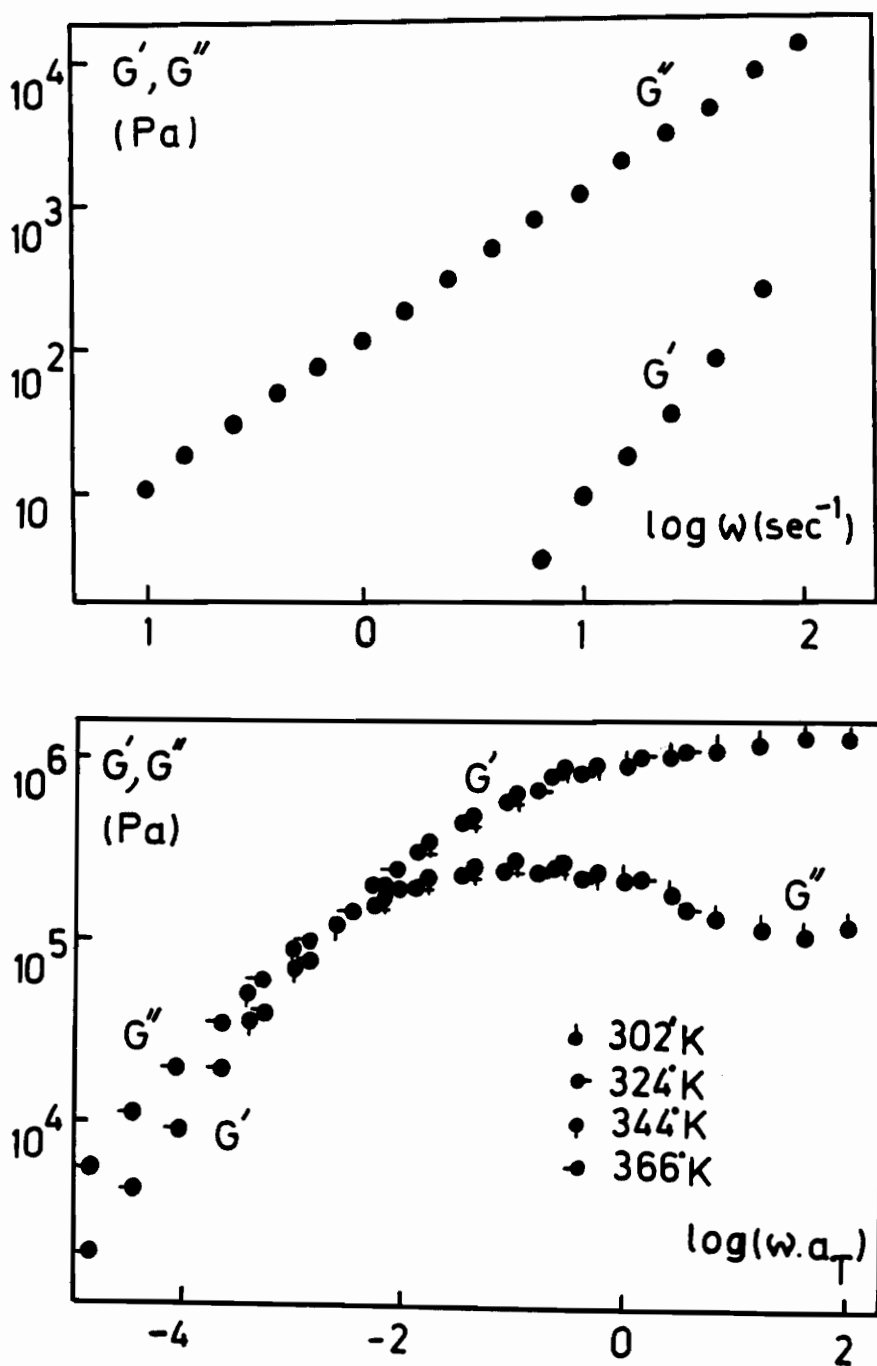


Figure 8. Dynamic behavior of carboxy-telechelic polybutadiene at 302K: (a) unneutralized form ($M_n = 4600$) and (b) master curve for same material neutralized with magnesium. From Broze et al. [75].

also controls the ionic content. Increasing the molecular weight decreases the ionic content. Figure 9 shows the effect of molecular weight on the viscoelastic behavior of both the carboxy-telechelic polyisoprene and the same material neutralized with magnesium. The unneutralized high molecular weight materials display a pseudo-rubbery plateau which disappears as molecular weight is decreased. In fact, the lowest molecular weight material ($\overline{M}_n = 7000$) could not be characterized due to its high fluidity. Upon neutralization, a dramatic change in behavior is observed. The 7000 \overline{M}_n material exhibits a rubbery plateau extending over several decades of frequency. With increasing molecular weight (decreasing ion content) the rubbery modulus decreases and the terminal region is shifted to higher frequency, indicating that a less extensive or weaker network is formed. Although the rubbery modulus is not strongly affected from 7000 to 20,000 \overline{M}_n , it decreases substantially when the molecular weight is further increased to 36,000. This is, of course, due to the decreasing influence of the ionic groups as molecular weight is increased and the concentration of ionic groups is further decreased. The increase in the rubbery modulus and the shift of the terminal region to lower frequencies when the molecular weight increased to 69,000 is due to the development of a more extensive entanglement network. That is, the effect of entanglements on relaxation rate is more pronounced at higher molecular weights relative to the influence of ionic interactions.

Broze et al. [78,80] have also been able to crosslink carboxy telechelic polybutadiene using Group IVb metals such as titanium, zirconium, and cerium. In this case, a stoichiometric amount of the metal alkoxide is not sufficient to efficiently crosslink the system. In fact, it was found that one metal per carboxylate group must be added to react with each chain end. In the second step, the alkoxy groups are hydrolyzed to crosslink the chains. These crosslinks formed are more covalent than ionic due to the nature of the metal cations. From viscoelastic measurements, it is clear that zirconium

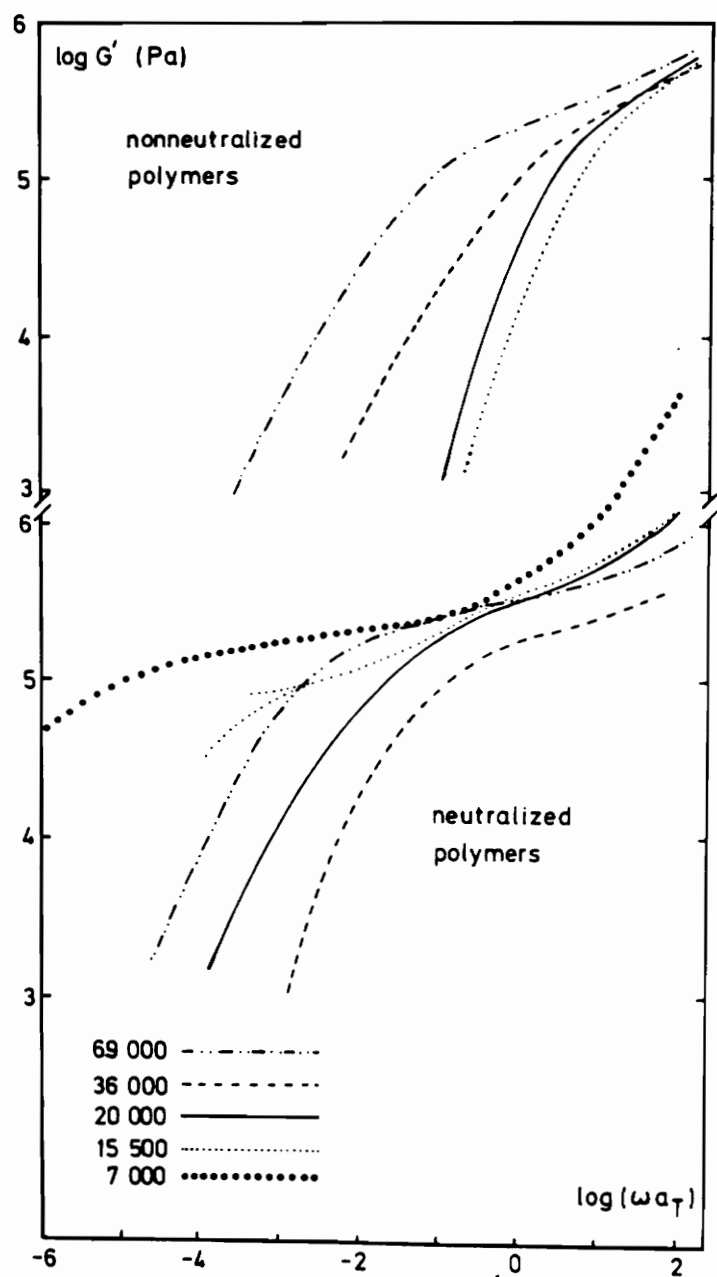


Figure 9. G' master curves for carboxy-telechelic polyisoprene: Effect of molecular weight and neutralization with magnesium. Reference temperature is 296K. From Jérôme and Broze [80].

is more efficient than titanium in crosslinking the carboxy-telechelic polybutadiene since the modulus is higher over the entire frequency range. According to the authors, this may be due to the larger ionic radius for zirconium (0.8 Å as compared with 0.68 Å for titanium).

Laleg et al. [81] studied the influence of cation valence on the viscoelastic transitions and microphase separation of carboxy-telechelic polybutadiene. Differential scanning calorimetry (DSC) was utilized to determine the amount of polybutadiene in the matrix rather than in the ionic aggregates. The heat capacity change ΔC_{p2} during the glass transition of the ionomer was measured and compared with the ΔC_{p1} of pure polybutadiene. Since any polymer chains within the ionic aggregates should not have sufficient mobility to undergo the glass transition, the value of $\Delta C_{p2} / \Delta C_{p1}$ was postulated to be related to the degree of microphase separation and $(\Delta C_{p2} - \Delta C_{p1})$ to the quantity of chains inside the ionic aggregates (multiplets and/or clusters) or in the interphase region between the ionic aggregates and polybutadiene matrix. The degree of microphase separation was found to be decreased by increasing the cation radius or by increasing the molecular weight of the oligomer. The data also suggest that excess neutralizing agent may also slightly decrease the degree of phase separation. In dynamic mechanical experiments this same variable caused the rubbery plateau to extend to higher temperatures and in some cases enhanced the rubbery modulus. Neither cation valence nor excess neutralizing agent was found to significantly influence T_g , confirming the results of Broze et al. [77]. Laleg and coworkers also observed a relaxation, appearing in the $\tan \delta$ curves, above T_g . This relaxation was attributed to the ionic phase and the temperature at which it occurs was found to depend upon the type of cation, decreasing with increasing cation radius.

Sulfonated Polyisobutylene Telechelic Ionomers.

Wilkes, Kennedy, and coworkers [82-89] have extensively studied the properties of sulfonated polyisobutylene telechelic ionomers. These materials have several advantages over the carboxylated telechelic elastomeric ionomers which were just discussed. First, the sulfonate groups are expected to provide stronger ionic bonding than the carboxylate groups, thus improving the mechanical properties. Second, the polyisobutylene chain is saturated and is thus more stable than the polybutadiene and polyisoprene based carboxylated ionomers. Third, a wider variety of chain microstructures have been made - specifically, linear monofunctional, linear difunctional, and three-arm star trifunctional.

It has been found that the three-arm star trifunctional materials possess the best mechanical properties of this series. This is due to the fact that each molecule already has a permanent covalent trifunctional network junction point. Clearly, only ion pair association should then be necessary for the formation of a three-dimensional elastomeric network. On the other hand, for the linear difunctional materials ion pair association would lead only to chain extension. Triplet or higher order associations would be necessary for network formation. The three-arm star trifunctional materials have been observed to sustain stresses in the range of 3-5 MPa and reach extensions of 800 to 1000% or more depending upon the molecular weight, neutralizing cation, and extent of neutralization (or excess neutralizing agent). By comparison, the linear difunctional materials rarely exceed 1 MPa stress and reach extensions of only 300-400%. Of course, the linear monofunctional materials cannot form a network and they are thus tacky, viscous fluids.

The effect of molecular weight upon the stress-strain behavior of the trifunctional materials neutralized with potassium hydroxide to the stoichiometric endpoint is shown in Figure 10. The nomenclature used in the figure can be illustrated by an example.

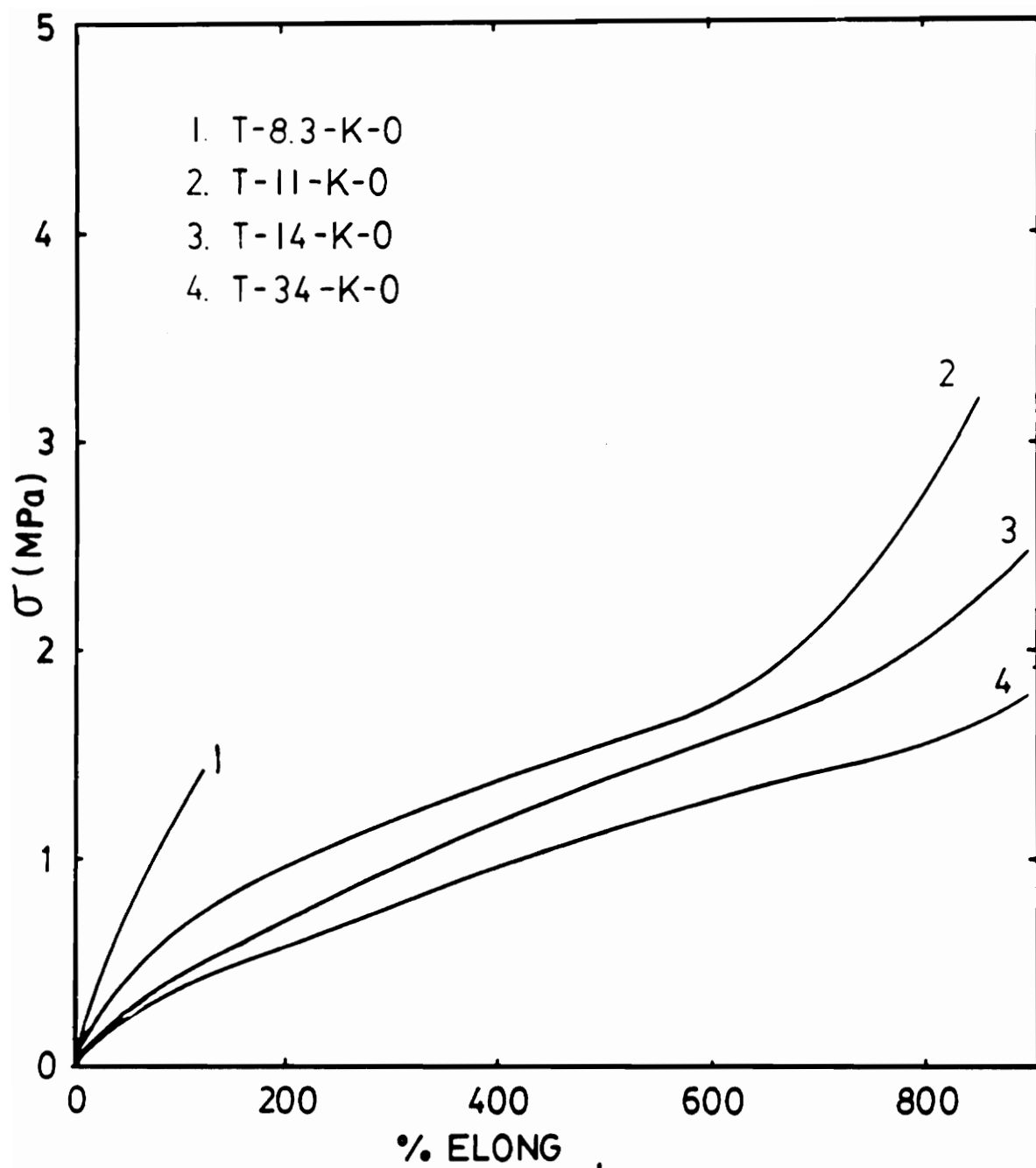


Figure 10. Stress-strain behavior of sulfonated PIB telechelic ionomers: Effect of molecular weight. From Bagrodia et al. [84].

T-8.3-K-0 indicates the trifunctional material of 8300 \overline{M}_n neutralized with KOH to the stoichiometric endpoint (or 0% excess neutralizing agent was added). Clearly, the stress is observed to increase as molecular weight decreases. This is due to the fact that, assuming only ion pair association occurs, the molecular weight between crosslinks decreases with decreasing arm length [84,89]. The upturn in stress above 600% elongation is due to strain-induced crystallinity as confirmed by wide-angle X-ray scattering patterns [83].

Another important finding has been the fact that excess neutralizing agent may strongly affect the mechanical properties of these materials [85]. Figure 11 shows how this variable influences the stress-strain behavior of the T-14-K series. The T-14-K-(-10) material, which was neutralized to only 90% (-10% excess neutralizing agent), does not reach 1 MPa stress or 800% elongation. Upon stoichiometric neutralization (T-14-K-0) the stress reaches almost 5 MPa and 1000% elongation. Thus it is clear that in order to achieve good mechanical properties, a stoichiometric amount of neutralizing agent must be added. There are further changes in the stress-strain behavior of this material as up to 300% excess neutralizing agent is added. This is in spite of the fact that the material, in solution, was steam-stripped three times prior to the final precipitation, drying, and mechanical testing. Thus the popular assumption that washing removes excess neutralizing agent is false. When neutralizing an ionomer, it is therefore important to be aware of how much neutralizing agent is added, since any excess is retained and strongly influences mechanical properties.

Carboxylated SBR.

Sato [90] has recently studied the ionic crosslinking of carboxylated SBR (styrene-butadiene-styrene rubber). SBR is a technologically important material whose proper-

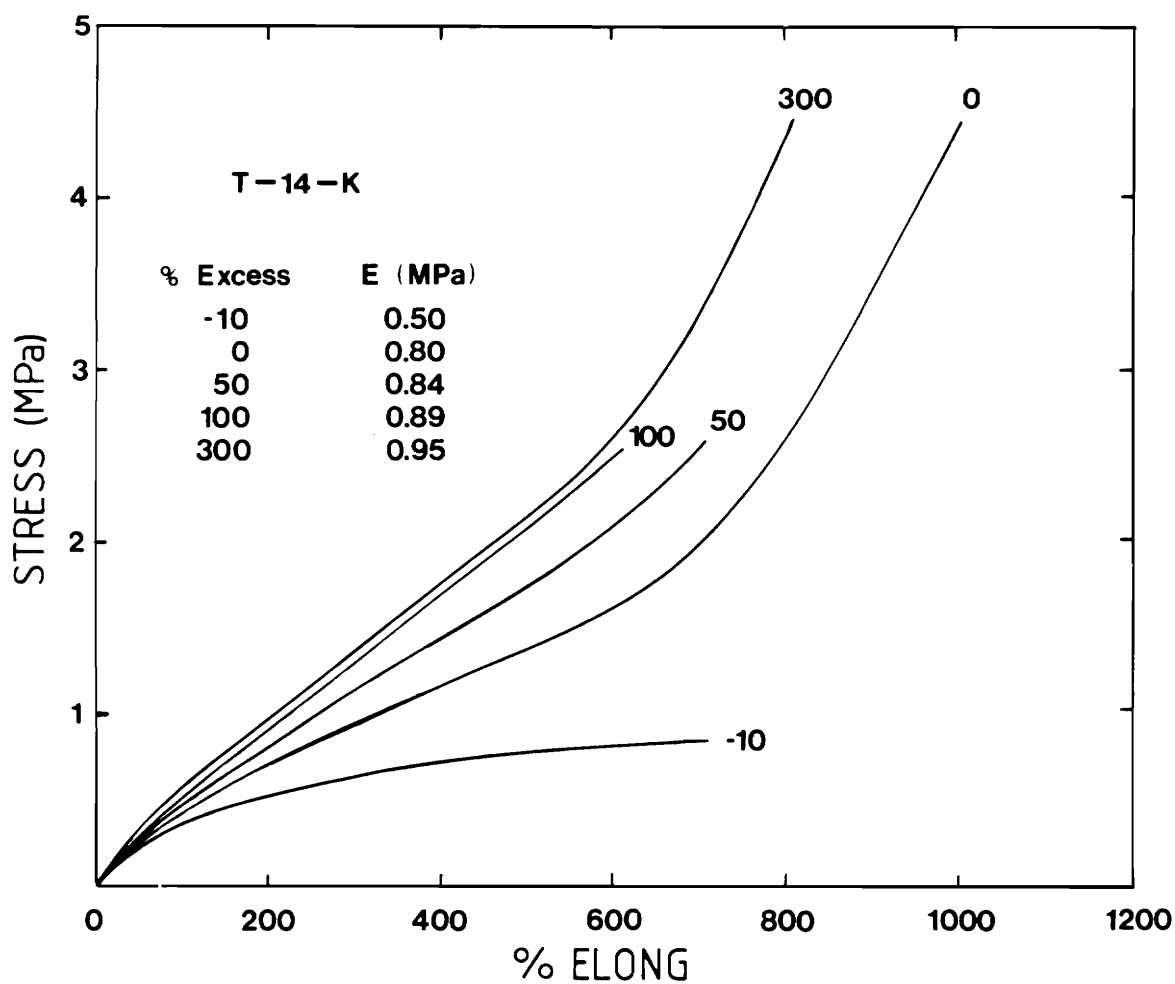


Figure 11. Stress-strain behavior of sulfonated PIB telechelic ionomers: Effect of excess neutralizing agent. From Mohajer et al. [85].

ties are often modified via covalent crosslinking at the unsaturation sites as well as by use of a filler such as carbon black. Carboxylated SBR is usually covalently crosslinked via reaction of the carboxylic acid groups with an appropriate reagent. Sato found that unneutralized carboxylated SBR displayed only a loss peak associated with the glass transition. Upon addition of zinc oxide, a higher temperature loss was observed at 40-60°C. This peak increases in intensity and shifts to higher temperatures with additional zinc oxide until a stoichiometric amount is present. Further addition of zinc oxide has little influence on the loss peak. The tensile strength was observed to increase and the ultimate elongation to decrease with zinc oxide content until the stoichiometric equivalence point was reached. Additional zinc oxide had no influence on these properties. The addition of carbon black (50 parts per 100 parts of rubber) shifts the peak 10°C higher, suggesting possible interaction of the carbon black and the ionic aggregates. The results of this work suggest that the utilization of ionic bonding could provide additional control over the properties of this technologically useful material.

Polyurethane Ionomers.

Cooper and coworkers [8,91-94] have extensively studied several types of novel polyurethane ionomers. Of course, polyurethanes function as thermoplastic elastomers due to the microphase separation which occurs. The hard domains which are glassy or semicrystalline serve as physical crosslinks as well as a reinforcing filler.

Hwang, Yang, and Cooper [8] prepared polyether-polyurethane zwitterionomers by reacting γ -propane sultone with the tertiary amine on the chain extender NMDEA (n-methyl diethanolamine) to give an ammonium sulfonate. The degree of sulfonation was altered by varying the amount of γ -propane sultone used. The calorimetric T_g was found to decrease and the transition zone narrow as the degree of ammonium sulfonation in-

creased, indicating that microphase separation is improved and the interfacial zone sharpened by the sulfonation. The effect of ammonium sulfonation level for a 37% hard segment (4,4-diphenyl methane diisocyanate (MDI)) system, where the ammonium sulfonation ranges from zero to 6.0% was studied by dynamic mechanical spectroscopy. It was found that increasing the sulfonation level decreases the soft segment glass transition temperature (as was also found by DSC) due to the improved phase separation. The rubbery plateau region is also enhanced due to both the improved phase separation and the fact that ionic bonding improves the cohesiveness of the hard microdomains. These materials were also found to be greatly strengthened by ammonium sulfonation.

These same zwitterionomers were converted to metal sulfonate ionomers by Miller, Hwang, and Cooper [91] by simply neutralizing the sulfonate groups with sodium acetate trihydride, zinc (II) diacetate dihydride, and iron (III) diacetate hydroxide. The quaternary ammonium was converted to a tertiary amine by loss of the methyl group. The dynamic behavior of two different series, a material with an interpenetrating hard domain structure and a material with isolated hard domains was studied. Control samples representing the material prior to formation of the zwitterionomer as well as the zwitterionomer itself were also studied. The material with the interpenetrating hard domains was found to be much more influenced by the type of ionic associations than the material with isolated hard domains. The rubbery plateau was enhanced by increasing the cation valence and was highest for the zwitterionomer. On the other hand, there was found to be very little effect on the rubbery modulus due to cation valence when the hard domains are more dispersed.

Rutkowska and Eisenberg [95-97] have also studied some aspects of the phase separation process in segmented polyurethanes utilizing a similar approach to Cooper and coworkers, i.e. the incorporation of NMDEA.

The fact that ionic bonding may be used to afford additional control of the structure and properties of such a technologically useful elastomer is certainly significant. Further work concerning the utilization of ionic bonding to modify the behavior of block and segmented copolymers could lead to a wider range of applications for these materials.

Behavior of Melts

It has already become clear that at higher temperatures ionic interactions are sufficiently reduced to allow flow of the material. The temperature at which this flow region begins depends upon such factors as chain flexibility, molecular weight, ionic content, ion and neutralizing ion type, and the level of added neutralizing agent. The importance of the thermal energy factor, kT , relative to the T_g of the polymer chain has been discussed. Of course, for flow to occur the temperature must be above the T_g of the chain backbone. Above the T_g , if there is insufficient kT to break up the ionic associations the material will behave as an elastomer as previously discussed. The kT factor increases with increasing temperature until the energy is sufficient to reduce the strength of the ionic associations enough for flow to occur. Although the material may flow in this temperature range, the ionic interactions still affect the flow behavior by acting similarly to temporary physical entanglements in high molecular weight melts. Also of importance is whether the ionomer is random or telechelic in nature. Given a similar ionic content for both types, the telechelic ionomer would normally be of lower molecular weight. If the molecular weight is also below the critical molecular weight for entanglements, then flow will be facilitated even further. In fact, this is one of the clear advantages of telechelic ionomers.

An example of how the incorporation of ionic groups effects the melt viscoelastic behavior is shown in Figure 12. In this work, Connelly et al. [98] studied the melt

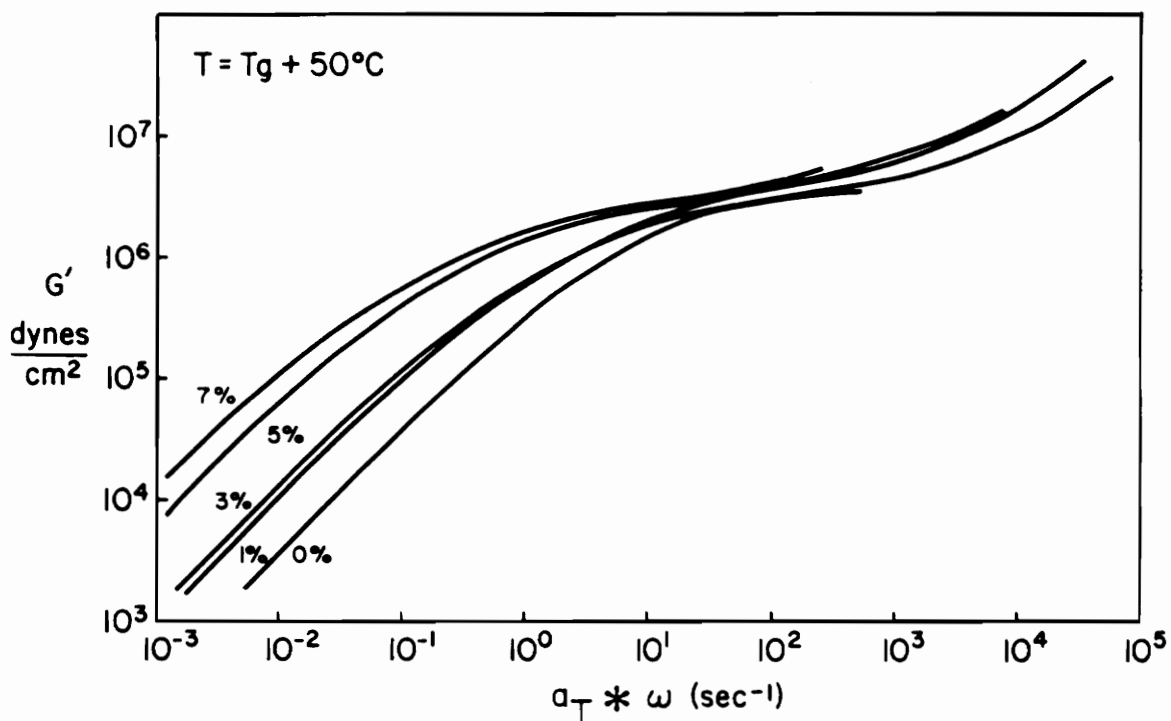


Figure 12. G' vs. frequency for a polyester ionomer: Levels of ionic content are as indicated and the reference temperature is $T_g + 50^\circ\text{C}$. From Connelly et al. [98].

rheology of a sodium-neutralized polyester ionomer in which the ionic content ranged from zero to 7 mole percent. The T_g was increased from 27 to 43°C with increasing ion content. Figure 12 shows the G' master curve for this series of materials at a reference temperature of $T_g + 50^\circ\text{C}$. Clearly, the effects of ionic content are seen primarily in the terminal or flow region, with G' increasing with increasing ion content. There is very little effect in the rubbery plateau region. The shift factors obey a WLF type of temperature dependence. This, of course, suggests that clustering does not occur at these ionic concentrations. It is interesting to note that in extensional flow, the behavior at small strains was not affected by ionic content. However, the strain at which the upturn in stress occurred was found to decrease with increasing ion content as might be expected. This is an area in which further work is certainly warranted.

The effect of the type of cation has already been discussed in some detail. Generally, materials resulting from neutralization with cations which form more covalent bonds (e.g. Zn^{2+}) will begin to flow at lower temperatures than those resulting from cations which form more ionic bonds (e.g. Ca^{2+}). Considering cations within a particular group of the periodic table, the strength of ionic associations increases with decreasing ionic radius. Thus the temperature at which melt flow begins can be controlled to a large extent through the choice of the neutralizing cation.

Bagrodia et al. [87,88] studied the viscoelastic behavior of the sulfonated polyisobutylene telechelic ionomers in the melt flow region. Figure 13 shows G' measured at 180°C for a series of the three-arm star trifunctional materials of varying molecular weight. The materials were neutralized with KOH, either stoichiometrically or with twice the stoichiometric amount as indicated in the figure caption. Clearly, at this temperature the storage modulus, G' , is observed to increase as \overline{M}_n increases from 8300 to 14000 to 34000 for the endpoint neutralized materials. Apparently at 180°C the ionic interactions are sufficiently weakened that molecular weight becomes the important

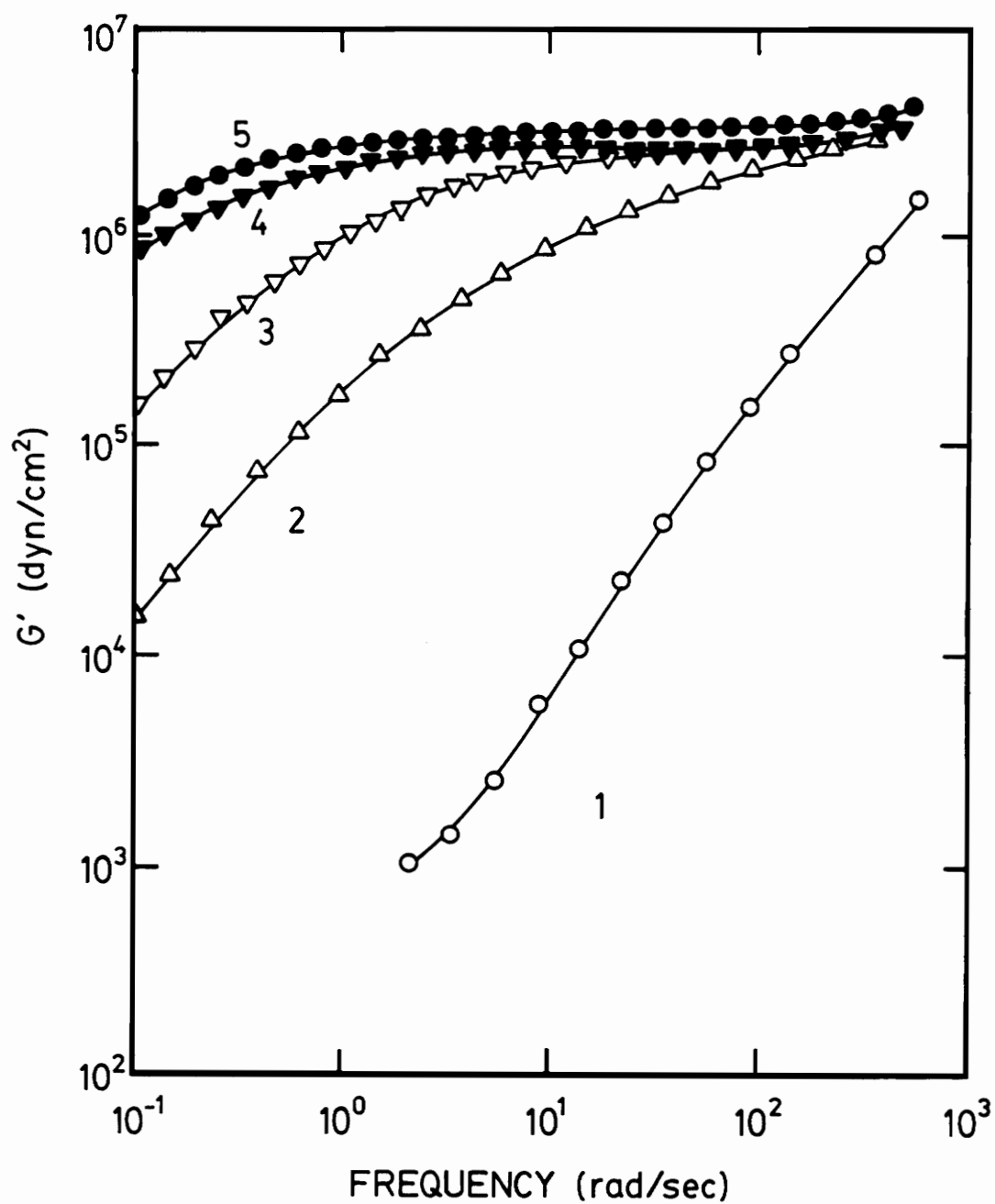


Figure 13. G' vs. frequency for three-arm star trifunctional ionomer: Neutralized with KOH and tested at 180°C : (1) T-8.3-K-0, (2) T-14-K-0, (3) T-34-K-0, (4) T-34-K-100, and (5) T-8.3-K-100.

factor. Since the number of entanglements increases with increasing molecular weight, G' is observed to increase with molecular weight. However, when 100% excess neutralizing agent is added, the ionic interactions are greatly strengthened and a dramatic increase in G' is observed at all frequencies, particularly for the 8300 \overline{M}_n material. In fact, for the materials with excess KOH, G' is higher for the 8300 \overline{M}_n material than for the 34000 \overline{M}_n material, indicating that the ionic content has again become the most important factor. The materials with excess KOH also behave as rubbery networks over the entire frequency range, while the endpoint neutralized materials do not. In fact, the 8300 \overline{M}_n material with a stoichiometric amount of KOH behaves as a viscous fluid even at the highest frequencies. The 14000 and 34000 \overline{M}_n materials undergo a transition from viscous flow to a rubbery network response at intermediate frequencies.

For materials of the random copolymer type with a similar ion content the molecular weight would typically be higher. At higher temperatures where ionic associations are weakened, the molecular weight and molecular architecture become the factors which contribute more to the viscoelastic response. The higher molecular weight of the random copolymer ionomer as opposed to the telechelic ionomer, as well as its linear architecture as opposed to the star architecture of the telechelic ionomer, result in the viscosity and storage modulus being higher. The large reduction in viscosity and storage modulus that the telechelic ionomers can achieve at elevated temperatures certainly increases their attractiveness when melt processability is an important consideration. Apparently, the variable of molecular weight has not been studied to any significant degree in the random ionomers even though its effects could be great, especially in the terminal region.

For the telechelic ionomers, the molecular architecture can also be a significant factor. Bagrodia et al. [88] found that the linear monofunctional sulfonated polyisobutylene telechelic ionomer of 11000 \overline{M}_n displays a near independence of shear

rate at 180°C. On the other hand, the linear difunctional and the three-arm star trifunctional species display shear-thinning with the trifunctional species showing a more pronounced reduction in viscosity with shear rate. This is as expected since the monofunctional species is below the critical molecular weight for entanglements and also cannot form a network. The difunctional and trifunctional species can form a network through ionic interactions, the network for the trifunctional material being more extensive. It is also of interest to note that the difunctional materials neutralized with zinc obey the time-temperature superposition principle while the analogous trifunctional materials do not.

As mentioned earlier, the solvation of ionic groups at elevated temperatures with a suitable ionic plasticizer such as zinc stearate reduces the ionic interactions and thus the viscosity and storage modulus. As would be expected, the degree to which these reductions in viscosity and storage modulus occur depends upon the amount of ionic plasticizer used. Thus, additional control over the properties in the melt flow region is afforded by use of these additives.

Behavior of Blends

Recently, Eisenberg and coworkers [95,96,99-102] have promoted complete or limited miscibility of immiscible systems by use of ionic interactions. They have taken two distinctly different approaches. In the first, a polymer which contains anionic groups is blended with another polymer containing cationic groups. For example, they have blended sulfonated cis-1,4-polyisoprene and styrene/4-vinylpyridine copolymers. The successful promotion of miscibility in this case was explained in terms of proton transfer from the sulfonic acid group to the vinylpyridine. While various techniques were applied to investigate this compatibilization, the dynamic mechanical behavior clearly verified

that miscibility was improved. A similar example from their work is the blending of sulfonated polystyrene with polyethylacrylate (PEA) containing vinylpyridine groups [100]. The dynamic mechanical behavior of a 50/50 blend of these two polymers without ionic groups is shown in Figure 14 and that for a 50/50 blend of the two polymers with ionic groups in Figure 15. It is clear that the blend of polystyrene and PEA was immiscible while the blend of sulfonated polystyrene and PEA with vinylpyridine groups is essentially completely miscible since only one T_g is observed.

Eisenberg and Hara [101,102] have also studied the use of ion-dipole interactions to promote miscibility. The materials studied were lightly sulfonated polystyrene and poly(alkylene oxides) such as poly(ethylene oxide) or poly(propylene oxide). These blends did display partial or complete miscibility. As expected, the polystyrene glass transition was depressed dramatically with increasing alkylene oxide content and the T_g of the alkylene oxide increases appreciably with increasing sulfonated polystyrene content. Furthermore, increases in sulfonate content at constant polystyrene levels also enhanced miscibility.

The idea of utilizing ion-containing polymers is a very interesting approach to expanding the range of new miscible blends. However, there is a need for studies which address the topics of multiplet and cluster development in these blended materials. One might question whether it would be easy to develop a cluster morphology in a blend of two ionomers that associate strongly but whose other chain segments are highly immiscible. It would seem that if the cluster is really a large aggregate of multiplets which incorporates portions of the chain backbone, this would not be a favorable situation. Thus investigations utilizing SAXS and related analytical tools to detect the presence of multiplet and cluster morphologies in these materials may be desirable. Such studies should also help shed light on questions which remain unanswered concerning single component systems.

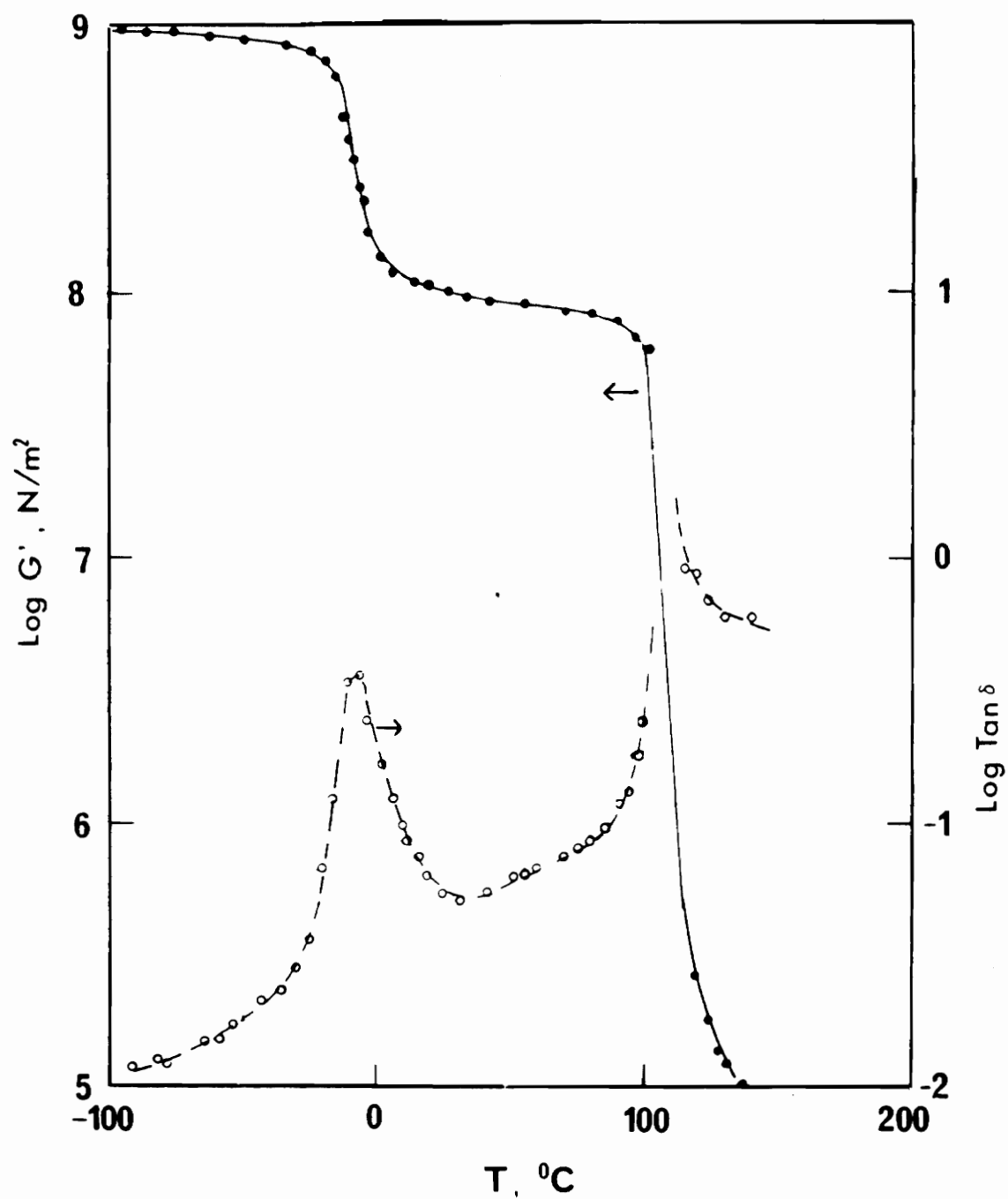


Figure 14. G' vs. temperature for a 50/50 blend of polystyrene with poly(ethyl acrylate): From Zhou and Eisenberg [94].

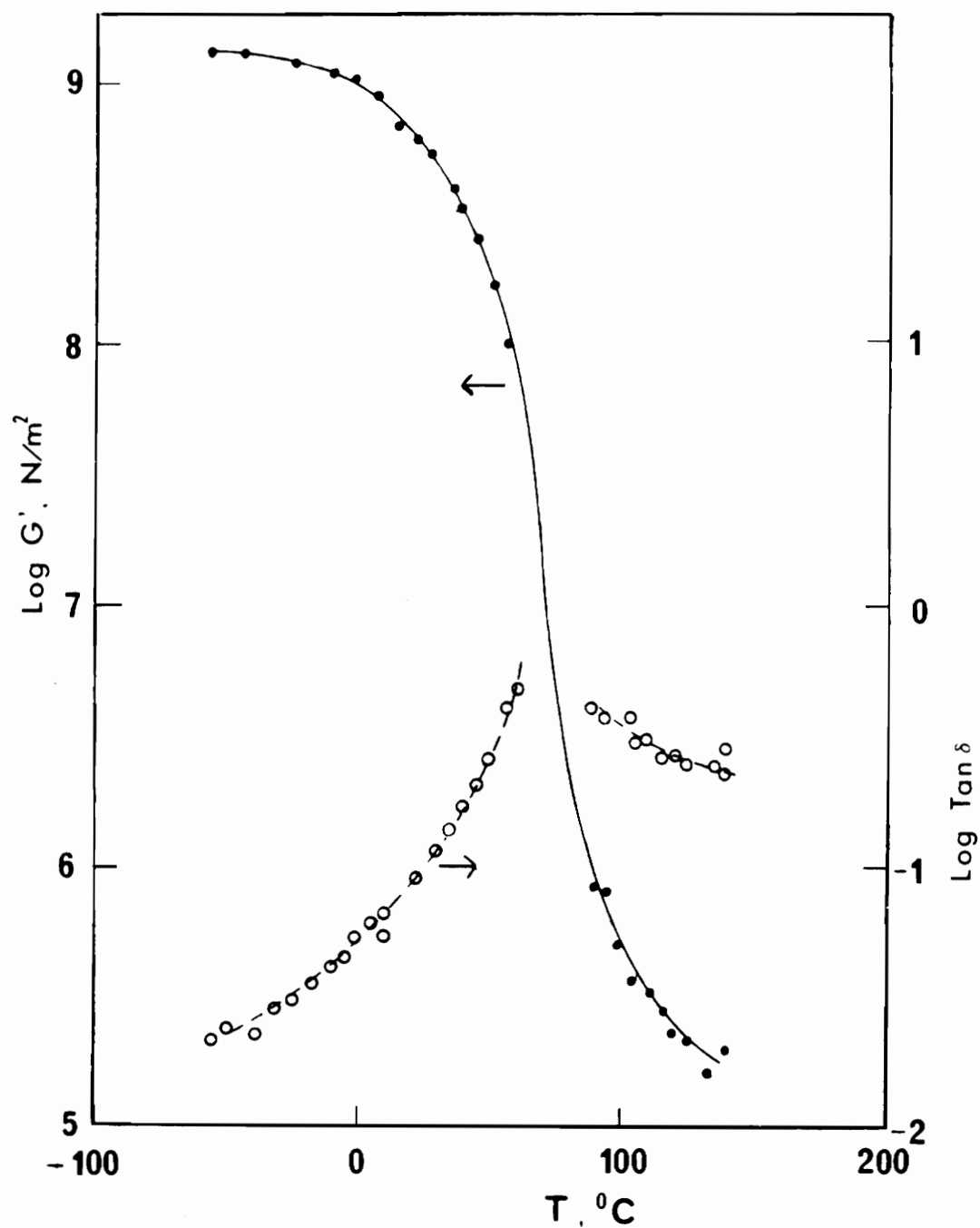


Figure 15. G' vs. temperature for a 50/50 blend of sulfonated polystyrene and poly(ethyl acrylate) containing vinylpyridine: From Zhou and Eisenberg [94].

Rheological Behavior of Ionomer Solutions

Although the bulk structure and properties of ionomers have been studied extensively, relatively little effort has been directed at developing an understanding of their solution behavior. This is in spite of many potential applications such as viscosity control agents and gelling agents for tertiary oil recovery. A recent paper by Dieterich [103] reviews the applications of polyurethane ionomers in aqueous dispersions and emulsions. Lundberg [104] has also considered the use of ionomers as fluid additives.

In addition to the need for research on ionomer solutions due to potential applications, such studies can also shed light on certain phenomena which affect the bulk structure and properties of ionomers. While segment-segment interactions are significantly reduced when an ionomer is diluted, the level of interaction between the ionic groups can be controlled by the choice of solvent. In nonpolar solvents the ionic groups are strongly attracted to one another, the apparent molecular weight is high, and thus the viscosity is high. As the polarity of the solvent is increased, the interaction of the solvent with the ionic groups increases. This decreases the association of the ionic groups on the polymer chains, decreasing the apparent molecular weight and thus the viscosity. Clearly, since at least 85% of the ionomer chain is nonpolar or relatively so, it may not be soluble in highly polar solvents. But ionomers may often be dissolved in nonpolar-polar solvent mixtures in which the content of a polar solvent, e.g. an alcohol, is very low. Such solutions may display quite unusual temperature effects as will be seen later.

This discussion of ionomer solution behavior will first focus on their viscometric behavior in nonpolar and polar solvents and nonpolar-polar solvent mixtures. Attention

will then turn to the dynamic behavior, particularly of ionomer solutions and gels in nonpolar solvents.

Viscometric Behavior

Nonpolar solvents.

Ionomers dissolved in nonpolar solvents associate very strongly due to the low polarity of the medium. Lundberg and Phillips [105] have shown that sulfonated polystyrene dissolved in tetrahydrofuran (THF) shows two different types of behavior, depending upon the concentration of the solution, as illustrated in Figure 16. At low concentrations the reduced viscosity of the sulfonated polystyrene solution is lower than that of the pure polystyrene solution and decreases with increasing level of sulfonation. In this low concentration region, intramolecular interactions predominate and the polymer coils are thus contracted. The viscosity is therefore reduced. As concentration increases, more intermolecular interaction occurs and the viscosity thus increases, becoming greater than that for the pure polystyrene solution and increasing with increasing level of sulfonation.

Broze, Jérôme, and Teyssié [106-108] have extensively studied the dilute solution behavior of carboxylated elastomeric telechelic ionomers based on polybutadiene and polyisoprene. Figure 17 shows a relative viscosity vs. concentration plot for carboxy-telechelic polyisoprene of $7000 \overline{M}_n$ in toluene both prior to neutralization and following neutralization with magnesium. The unneutralized form displays a relative viscosity whose concentration dependence is typical of that for a low molecular weight polymer in solution. However, upon neutralization with magnesium there is a very sharp increase

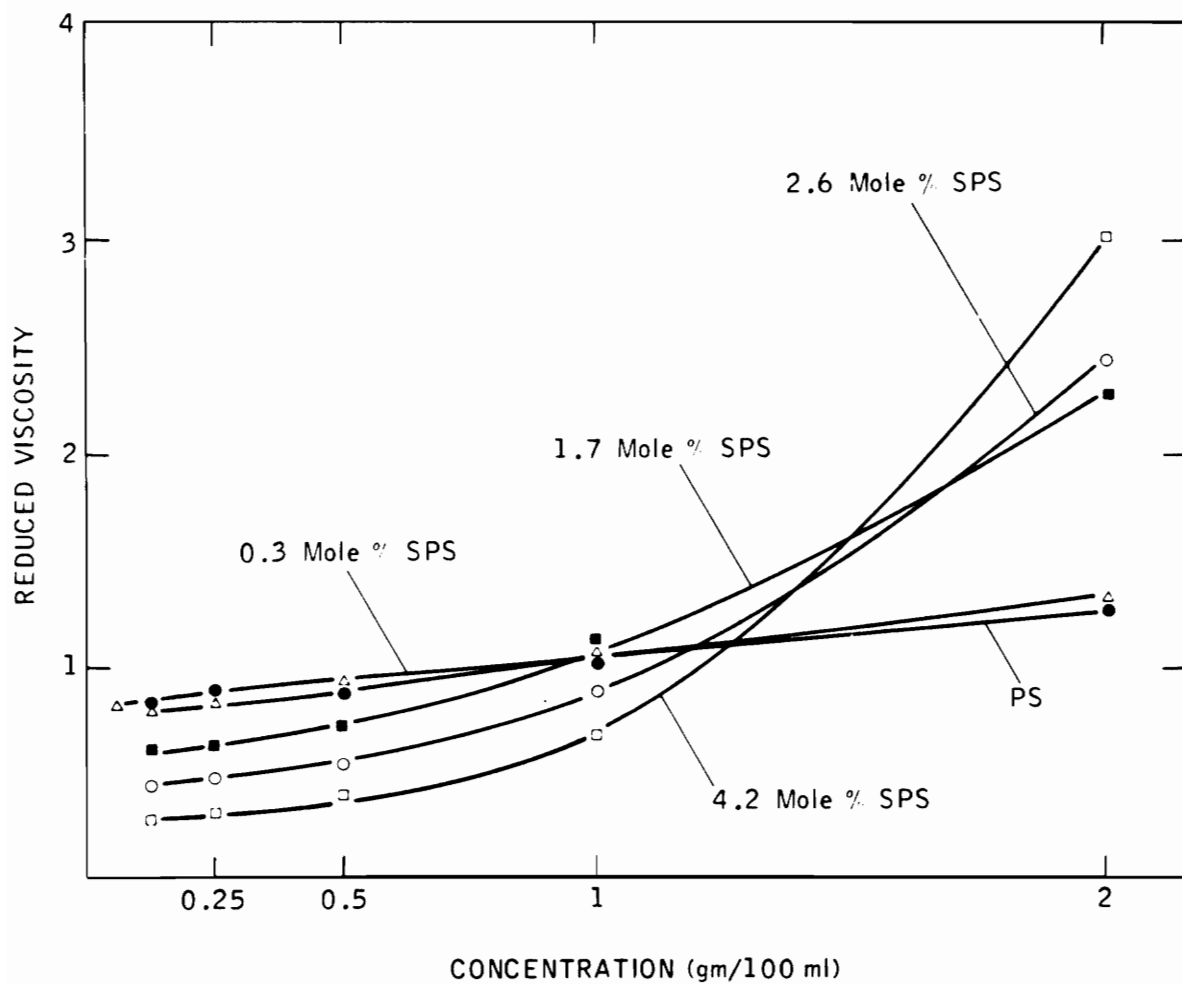


Figure 16. Reduced viscosity vs. concentration of sulfonated PS in THF: Neutralized with sodium. Sulfonation levels are as indicated. From Lundberg and Phillips [105].

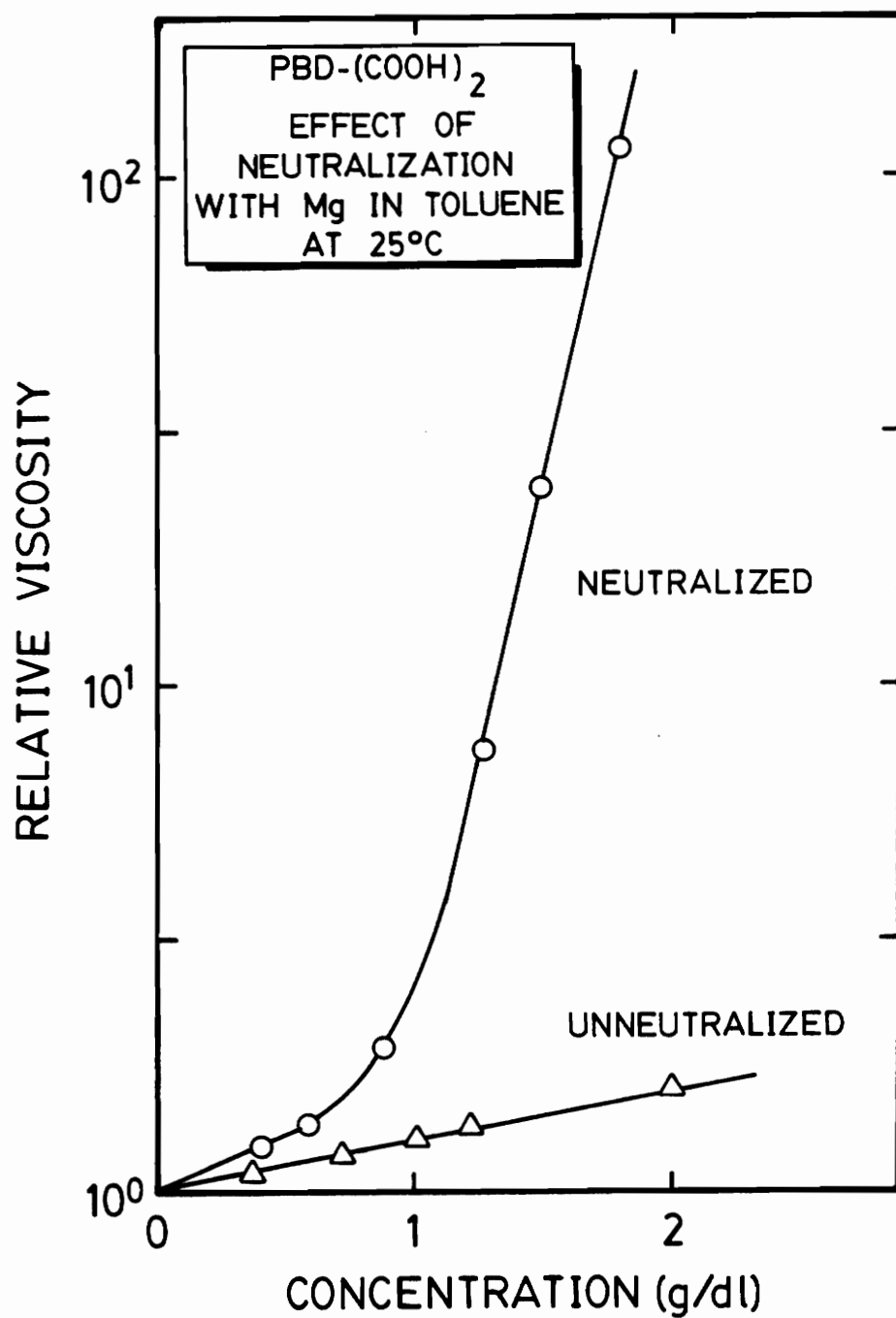


Figure 17. Effect of neutralization with magnesium on relative viscosity of carboxy-telechelic polyisoprene: $\bar{M}_n = 70,000$. At 25°C. From Broze et al. [106,107].

in relative viscosity at about 1.5 g/dl which Broze et al. refer to as gelation. Of course, this dramatic viscosity increase is a result of the intermolecular association of the Mg carboxylate groups which increase the apparent molecular weight and thus the viscosity. The gelation was observed to be strongest for the Mg cation and decreased in the order $Mg > Ca > Ba > Cu > Mn$. More polar solvents and higher temperatures were found to decrease the gelation effect as would be expected. As shown in Figure 18 the gelation concentration was found to decrease with increasing molecular weight. Broze et al. [108] theoretically derived an equation to account for this behavior. This equation states that the gelation concentration is inversely proportional to the square root of the number-average molecular weight, \overline{M}_n ; i.e.

$$C_{gel} = k\overline{M}_n^{-1/2} \quad [2.2]$$

where k is a proportionality factor. This equation has been found to fit the C_{gel} vs. \overline{M}_n behavior for several types of carboxylated telechelic ionomers in nonpolar solvents.

In the random type of ionomers viscosity increases with increasing ion content in nonpolar solvents. This behavior is opposite that predicted by equation (2.2) for telechelic ionomers. Equation (2) predicts that viscosity increases with increasing molecular weight. Joanny [109] has theoretically approached the problem of ionomer association in solution using scaling concepts. His prediction is that viscosity increases with increasing ion content as is found for the random ionomers. Forsman and Hong [110,111] have theoretically treated the problem using a statistical mechanical approach which considers only the formation of dimers. Their result agrees with the prediction of Joanny for low dimerization energies and with Broze et al. for higher dimerization energies. However, the reason for this limited agreement with the two other theories is

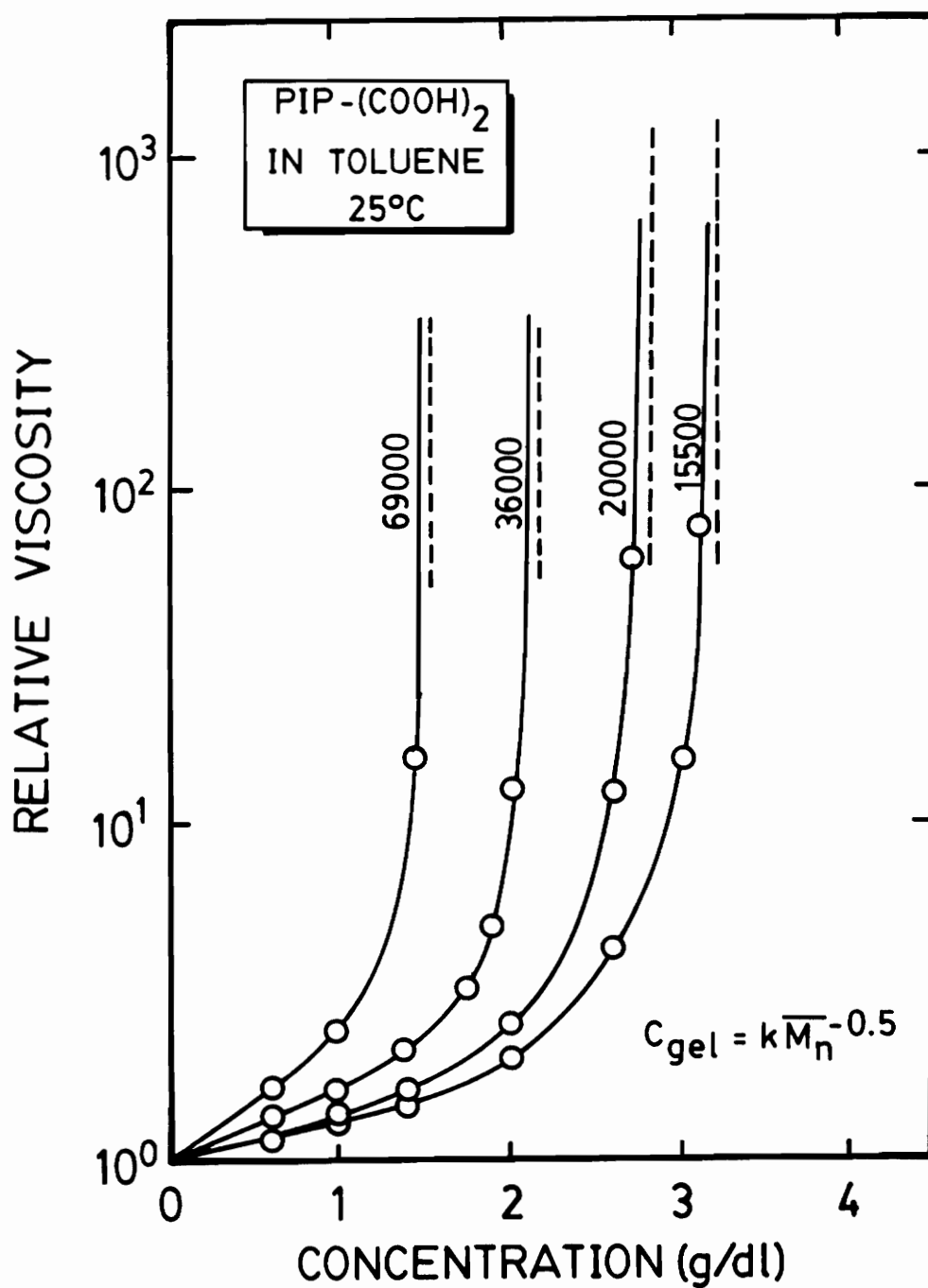


Figure 18. Effect of molecular weight on gelation behavior of carboxy-telechelic polyisoprene neutralized with magnesium: At 25°C. From Broze et al. [107].

not presently understood. Clearly, additional work will be necessary to gain a complete understanding of ionomer association in nonpolar solvents.

Polar solvents.

Relatively little work has been done on solutions of ionomers in more polar solvents due to their limited solubility in such an environment. However, Lundberg and Phillips [105] and Peiffer and Lundberg [112] have studied the viscometric behavior of sulfonated polymers in solvents such as dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). It was found that ionomers in these solvents display the typical polyelectrolyte effect at low concentrations, i.e. viscosity increases with decreasing concentration. The ionic groups are solvated by the polar solvent and thus repel one another quite strongly due to the high local charges. At low concentrations this mutual repulsion of like charges on the same chain thus expands the polymer coils and increases viscosity. Figure 19 shows such behavior for sulfonated polystyrene in DMF. It should be noted that the viscosity increases more dramatically for higher levels of sulfonation. Similar results have been found by Niezette, Vanderschueren, and Aras [113] and Rochas, Domard, and Rinaudo [114].

Nonpolar-polar solvent mixtures.

As mentioned earlier, ionomers dissolved in nonpolar solvents with a small amount of a more polar solvent, such as an alcohol, may display very unusual viscosity-temperature effects. Lundberg and Makowski [115] and Lundberg [116,117] have made extensive studies of such solutions. The viscosity of simple fluids, including typical

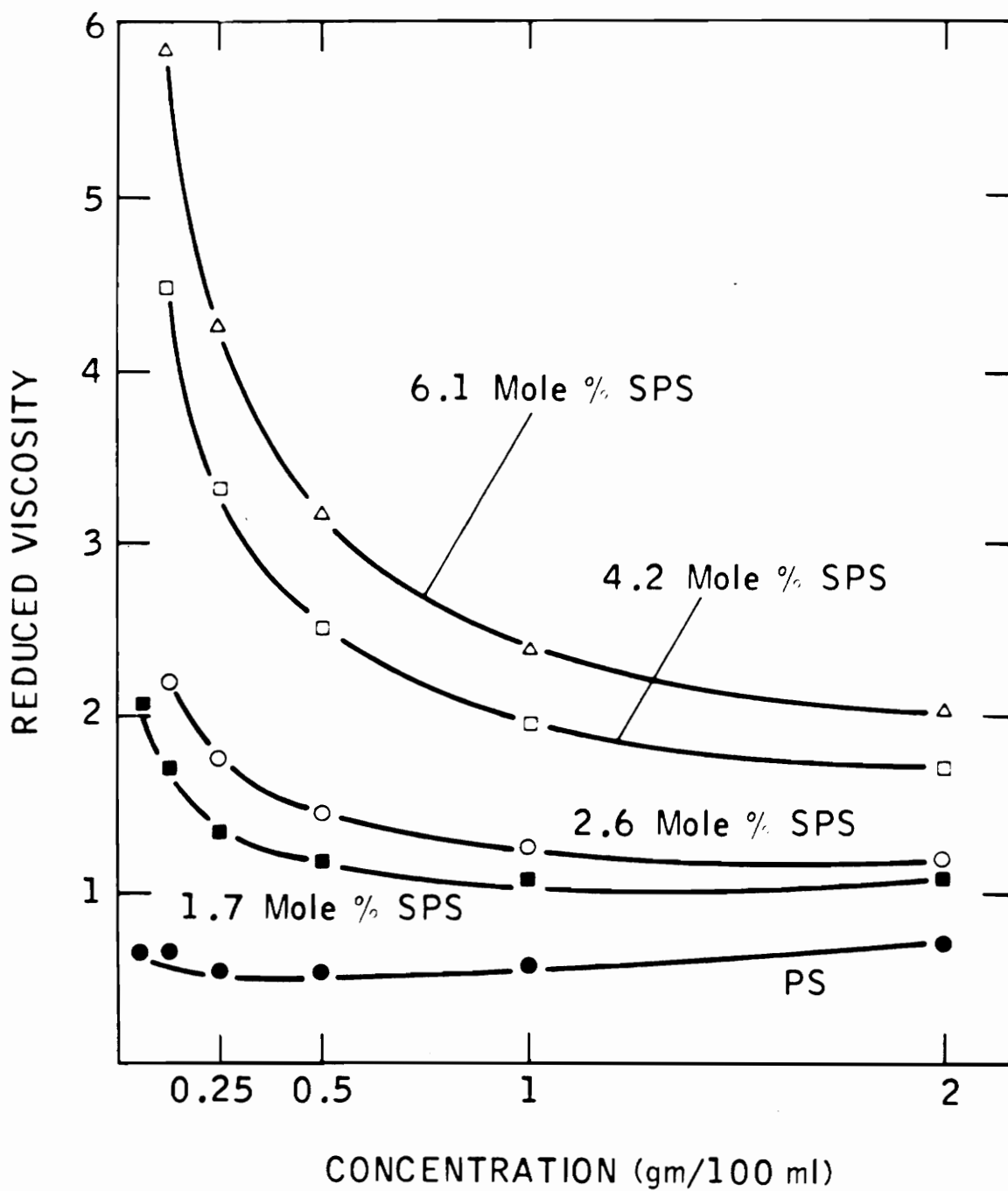
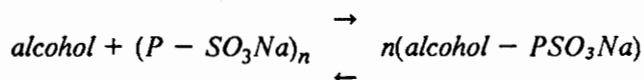


Figure 19. Reduced viscosity vs. concentration for sulfonated PS in DMF: Neutralized with sodium. Sulfonation levels are as indicated. From Lundberg and Phillips [105].

polymer solutions, decreases with increasing temperature. Typical examples are shown in Figure 20, where the temperature-dependent viscosity of 3% and 18% polystyrene in xylene is shown. Clearly, the viscosity is observed to decrease with increasing temperature as expected. Figure 21 shows the temperature-dependent viscosity of sodium sulfonated polystyrene (1.98 mole % sulfonate) solutions in xylene/hexanol mixtures. One is a 3% solution in a 3% hexanol/97% xylene mixture, and the other is a 5% solution in a 5% hexanol/95% xylene mixture. Both solutions show a dramatic increase in viscosity as temperature increases from 25 to 80°C. Lundberg and Makowski [115] interpret this behavior using the equilibrium



where the associating species ($P - SO_3Na$) is favored at high temperatures, while the solvated species ($alcohol - PSO_3Na$) is favored at low temperatures. These workers do admit that this is an oversimplification since it ignores the hydrocarbon solvent and the polymer backbone. At higher temperatures the strength of the ionic interactions is decreased and thus the viscosity begins to decrease again. Such unusual viscosity-temperature effects in mixed solvents have also been observed by Misra and Mandal [118].

Dynamic Behavior

The association of ionomers in nonpolar solvents results, not only in unusual viscosity behavior, but unusual dynamic behavior as well. Agarwal and Lundberg [119] have studied the behavior of sulfonated EPDM in a paraffinic oil. Figure 22a shows the viscoelastic behavior of a 5% solution of zinc sulfonated EPDM in a paraffinic oil. It

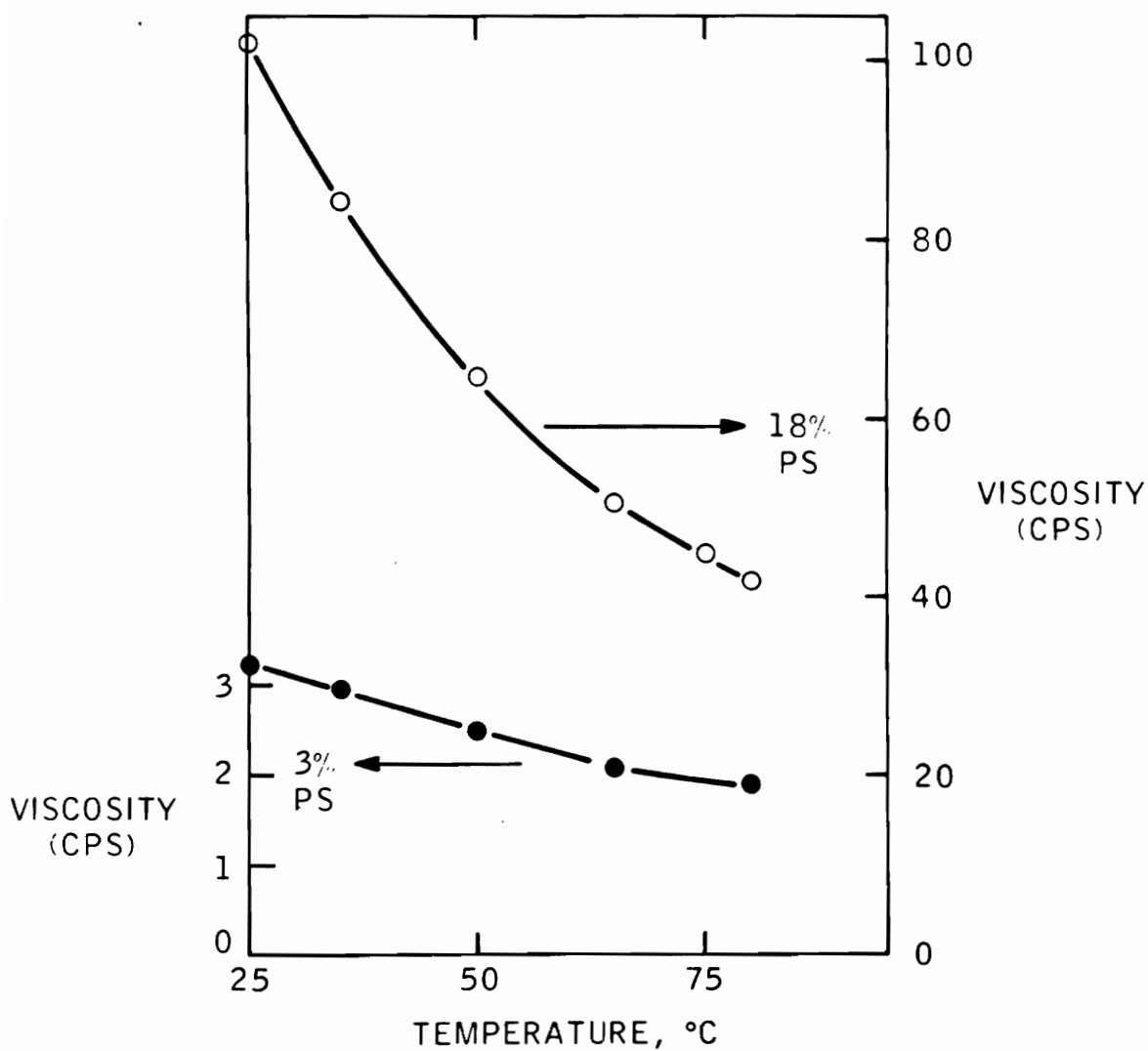


Figure 20. Viscosity-temperature behavior of 3% and 18% polystyrene in xylene: From Lundberg and Makowski [115].

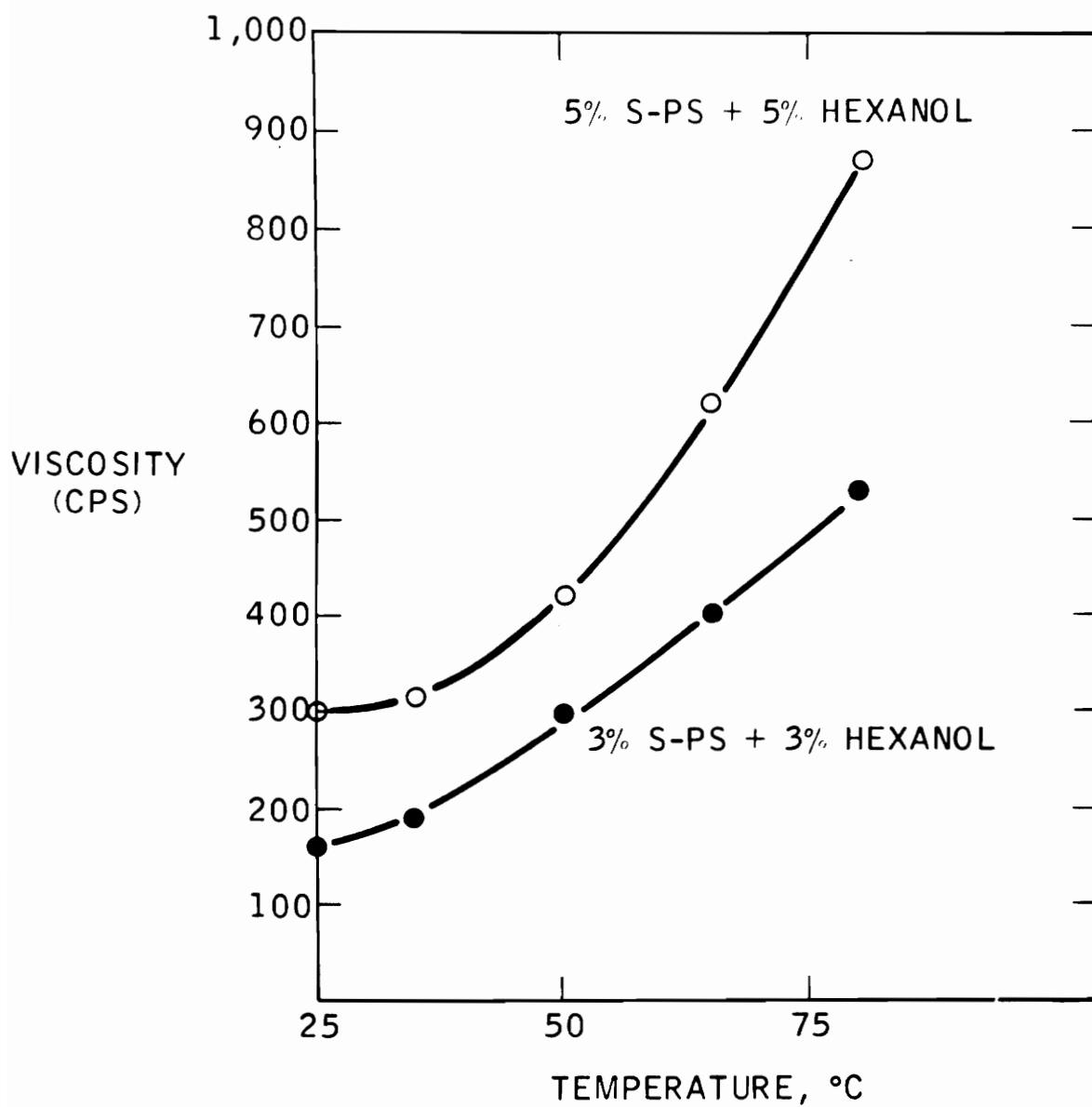


Figure 21. Viscosity-temperature behavior of sulfonated polystyrene (1.98 mole %) in xylene/hexanol: 3% solution in 3% hexanol/97% xylene and 5% solution in 5% hexanol/95% xylene. From Lundberg and Makowski [115].

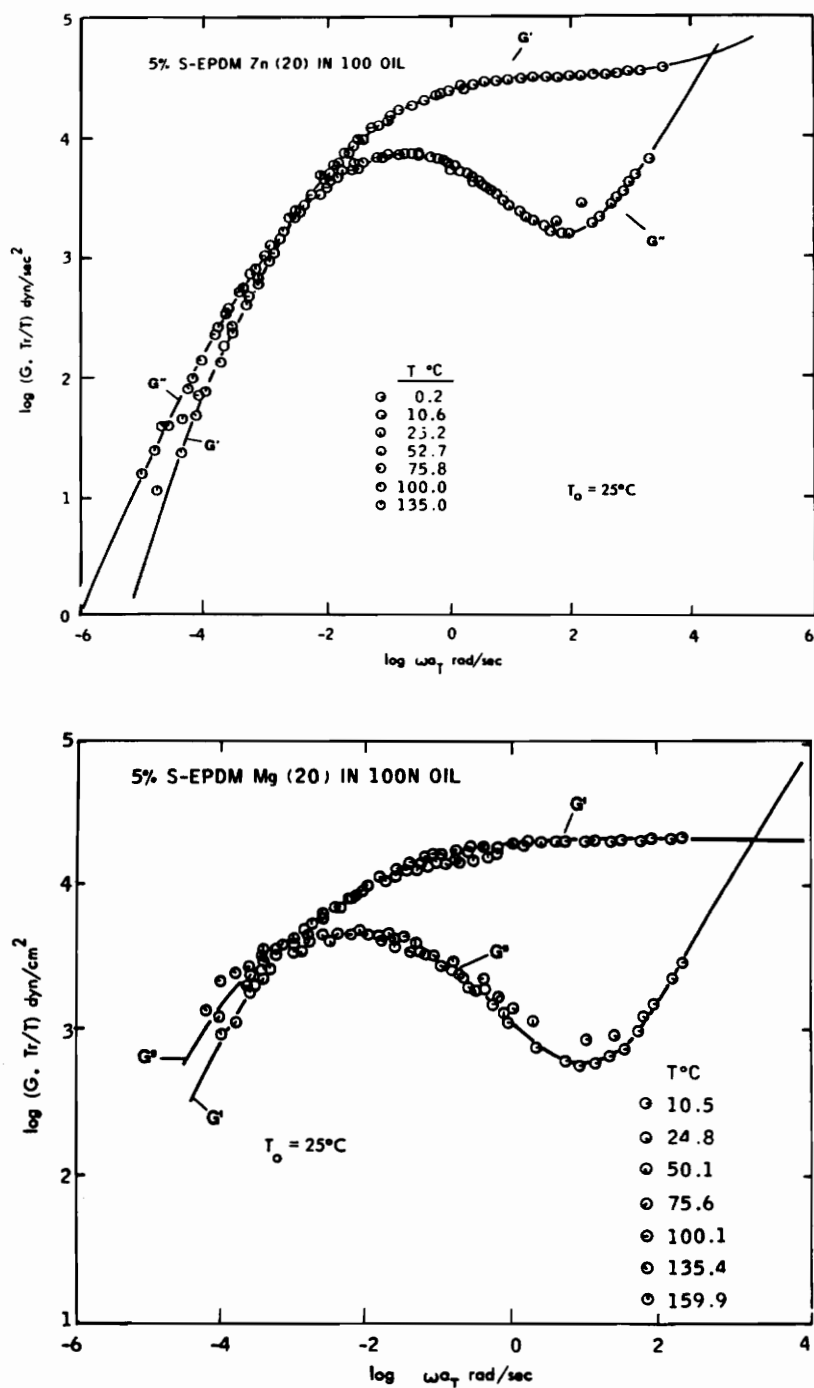


Figure 22. G' and G'' vs. frequency for zinc sulfonated EPDM's: (a) 5% sulfo-EPDM Zn salt in 100N oil and 5% sulfo-EPDM Mg salt in 100N oil. Reference temperature is 25°C . From Agarwal and Lundberg [119,120].

should be noted that in the low frequency region, the G' curve (G' vs. $\log \omega a_i$) has a slope of 2 and the G'' curve has a slope of 1. These are the slopes that are theoretically predicted for a linear viscoelastic fluid. As frequency is increased, the fluid begins to behave more as an elastic network as indicated by the relatively constant G' and decreasing G'' . At very high frequencies G'' again increases, apparently anticipating another transition which would be observed only at higher, experimentally inaccessible frequencies or at lower temperatures. This master curve was constructed by shifting curves obtained at the various temperatures indicated in Figure 22a.

Similar experiments on solutions of sulfonated EPDM neutralized with magnesium and barium show that these solutions display a much more network-like response due to the stronger association of ionic groups [120]. Although time-temperature superposition failed for these solutions, pseudomaster curves of G' and G'' were constructed. These curves, shown in Figure 22b, illustrate that the low frequency limiting slopes are not reached within the experimentally accessible values of temperature and frequency, and that the network-like response is observed over a wider range of frequencies. The failure of time-temperature superposition is also apparent.

As was discussed earlier, a small amount of a polar cosolvent can cause the viscosity to increase with increasing temperature. Agarwal, Garner, and Lundberg [121] have studied the viscoelastic behavior of such solutions. For a 2% solution of magnesium sulfonated EPDM (0.67 mole % sulfonate groups) in a solvent mixture consisting of 98.5% paraffinic oil and 1.5% hexanol, an increase in G' is observed at all frequencies as temperature is increased in the range of 22.3 to 75.9°C. This would be expected, of course, from the viscosity behavior. At room temperature the behavior of G' and G'' approaches that of a Newtonian solution, while at 75°C they display a network-like response. The curves are also not superposable.

Broze et al. [122] have studied the viscoelastic behavior of solutions of carboxylated polybutadiene telechelic ionomers in decalin. These materials all had a number average molecular weight of 4600. At a concentration of 10 g/dl, magnesium-neutralized solutions display a shear-thickening behavior due to the dynamic nature of the ionic interactions. At low shear rates the characteristic flow time is greater than the average lifetime of the ionic associations so that they are only felt as temporary crosslink points with an effect similar to that of entanglements. As shear rate is increased the characteristic flow time decreases, finally becoming shorter than the average lifetime of the ionic associations. The ionic associations are then felt more strongly, the crosslink density increases, and the viscosity increases. Witten and Cohen [123] have recently proposed a quantitative theory which predicts such behavior. The dynamic behavior of these solutions is highly dependent upon the cation used to neutralize the carboxylic acid groups. The curves for G' and G'' are superposable, at least in the temperature range between 297 and 342K, and the shift factors obey an Arrhenius type of dependence. For this series of materials neutralized with alkaline earth cations, the elasticity of the solutions increases with decreasing cation size. It should be mentioned at this point that not all ionomer solutions display shear thickening. Agarwal and Lundberg [119] have observed shear-thinning behavior for sulfonated ionomer solutions. This difference in shear rate dependent behavior is certainly an area in which further work is necessary.

Gonzalez [124,125] has theoretically approached the problem of predicting the viscosity and viscoelastic behavior of ionomer gels. By regarding the system as a polymer solution with transient crosslinks, he was able to derive an expression for the viscosity of ionomer gels using reptation arguments. The stress relaxation tensor was calculated and, assuming shear flow, the values of the dynamic moduli G' and G'' were calculated by using the classical equations from viscoelastic theory. Plots of the calculated G' and G'' are shown in Figure 23. Clearly the terminal region shows G' with a

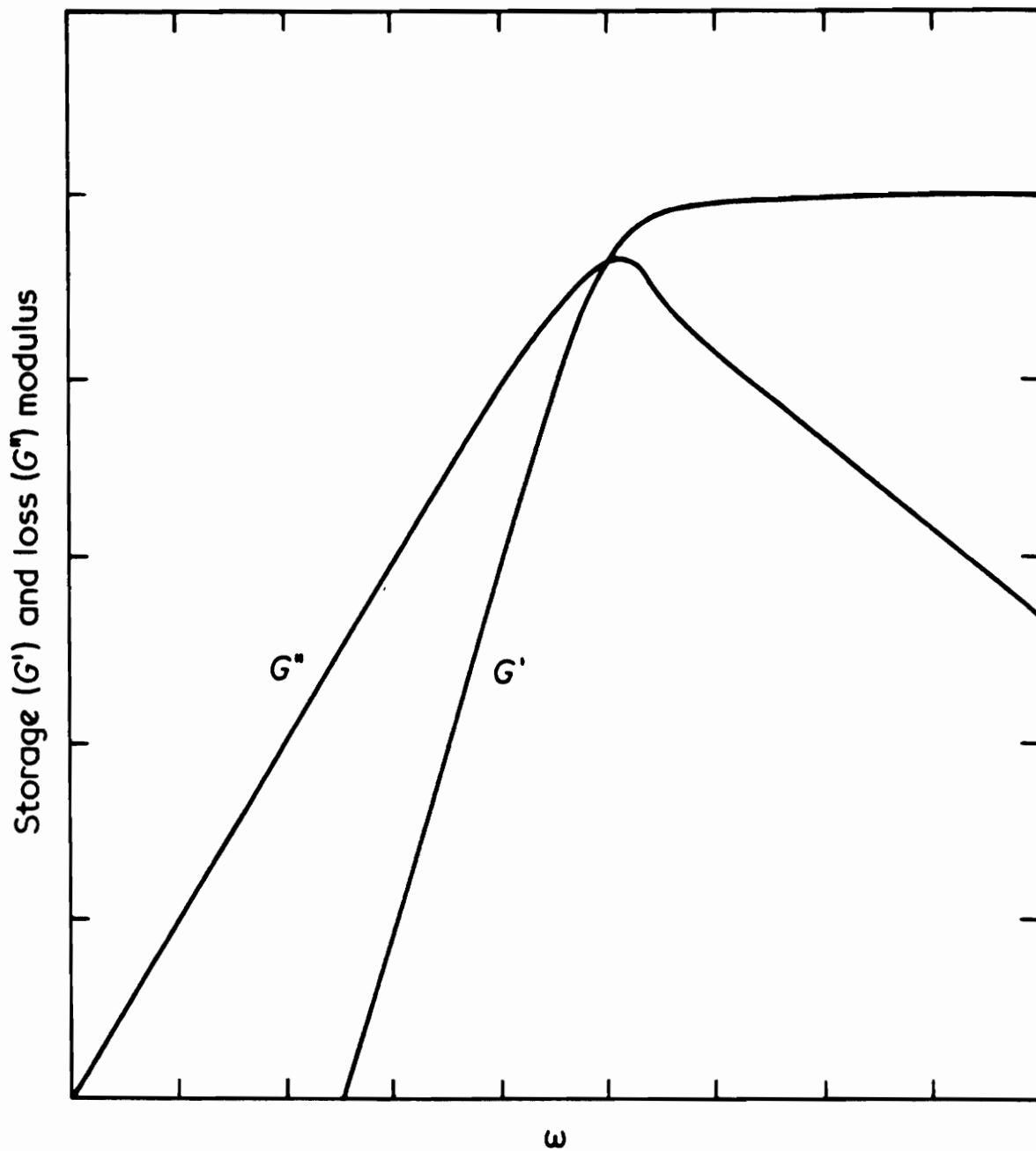


Figure 23. Predicted G' and G'' behavior for an ionomer gel: From Gonzalez [125].

slope of 2 and G'' with a slope of 1 as predicted for a linearly viscoelastic fluid. At a certain critical frequency, G' reaches a plateau and G'' goes through a maximum. This behavior is qualitatively very similar to that found by Agarwal and Lundberg for sulfonated EPDM solutions (see Figure 22).

III. Purpose and Scope of Present Work

Bulk Structure and Properties of Sulfonated Polyisobutylene Telechelic Ionomers

As was discussed at length in the previous chapter, the morphological structure of the ionic aggregates in ionomers is not yet well defined. One of the attractive features of telechelic ionomers, of course, is that the chain microstructure is well-defined and regular, thus potentially leading to a more regular arrangement of the ionic aggregates. Previous structural studies of the carboxy-telechelic ionomers by small-angle X-ray scattering has suggested that these materials may form more layer-like or lamellar type structures rather than the spherical clusters postulated for random ionomers [17-20]. It was thus believed that similar studies on the sulfonated polyisobutylene telechelic ionomers would provide an interesting comparison. However, initial SAXS studies on these materials prior to the time the author joined the project indicated that the expected "ionic peak" was not present even at the highest ion concentrations, i.e. the lowest molecular weights. SAXS experiments were also run using the synchrotron radiation facility at Stanford University with similar results - no clear SAXS peak. Even though both sets of experiments failed to show the SAXS peak, this result was somewhat perplexing. Based upon the SAXS experiments on carboxy-telechelic ionomers, it seemed that the low molecular weight sulfonated polyisobutylene telechelic ionomers should also show

an ionic peak. In the meantime, the SAXS apparatus in our laboratory was equipped with a position sensitive detector (PSD). Following the installation of the PSD, further SAXS studies of the sulfonated polyisobutylene telechelic ionomers were made with some quite interesting results. Some of these results are presented here.

In the work of Bagrodia et al. [89] stress relaxation experiments at ambient conditions indicated that apparent equilibrium stress values are reached within about an hour or so for the three-arm star trifunctional ionomers but not for the linear difunctional ionomers. One of the goals of this work was to determine whether or not this apparent equilibrium is indeed a true equilibrium or if further relaxation occurs at longer times as would be expected. Such information could be extremely important in applications which would require the material to sustain a load for long periods of time.

In prior work on the sulfonated polyisobutylene telechelic ionomers, the sulfonic acid groups were neutralized only with monovalent (K^+) and divalent (Ca^{2+} and Zn^{2+}) cations. For the case of monovalent cations, ion association may be limited to dipole-dipole interactions resulting in only chain extension. Although some higher order associations are likely, they may be small in number depending upon the ion content. For the divalent cations, if each divalent cation associates with only two sulfonic acid groups, then again only chain extension would occur. If neutralization with a trivalent cation is considered, one might expect that in the absence of steric hindrance each cation could associate with three sulfonic acid groups to form a trifunctional ionic crosslink. One of the objectives in this work was to neutralize the sulfonated polyisobutylene telechelic ionomers with trivalent cations such as La^{3+} and Ce^{3+} , and to compare the properties of these materials with those of materials neutralized with monovalent and divalent cations. It was suspected that such materials may display greater strength as well as enhanced network stability.

In previous work on the sulfonated polyisobutylene telechelic ionomers, it was found that the materials are too soft (i.e. they tend to flow at higher temperatures) to allow adequate study of their viscoelastic behavior using the Rheovibron instrument normally used for this purpose. Since the Rheovibron operates in the tensile mode, any tendency of the material to flow results in it being impossible to maintain adequate tension on the specimen. The new Polymer Laboratories DMTA instrument can be operated in the shear mode, which makes it possible to study the viscoelastic properties of such slowly flowing materials. This instrument was therefore used to study the viscoelastic behavior of the sulfonated polyisobutylene telechelic ionomers.

Solution Behavior of Sulfonated Polyisobutylene Telechelic Ionomers

The unique properties of ionomer solutions, as discussed in the previous chapter, suggest that ionomers may serve as useful viscosity control agents, gelling agents for tertiary oil recovery, etc. It is therefore of importance to characterize the structure-property behavior of ionomer solutions so that this knowledge may be used to design specific ionomers for these potential fluid applications. As mentioned earlier, study of ionomer solution behavior also provides another way to obtain information about ionic interactions in specific environments which might also be applied to bulk ionomers. The studies of Broze et al. [106-108] on the solution behavior of carboxy-telechelic ionomers have revealed much about the association of ionomers in solution due to the controlled and specific molecular characteristics of these materials. An objective of the present work was to study the solution behavior of sulfonated polyisobutylene telechelic ionomers using an approach similar to that of Broze et al. As compared to the carboxy-telechelic ionomers, the sulfonated polyisobutylene telechelic ionomers make

available a broader range of chain microstructures as well as sulfonate terminal groups instead of carboxylates. It is certainly of importance to understand exactly how these molecular variables affect solution behavior. The variables of interest include molecular architecture, molecular weight, neutralizing cation, excess neutralizing agent, etc. Also of importance is the polarity of the solvent. Lundberg and Phillips [105] found that sulfonated polystyrene solutions behave quite differently depending upon the polarity of the solvent. Similar effects might be found in the sulfonated polyisobutylene telechelic ionomers. It was realized, however, that their solubility in more polar solvents would be limited due to the low concentration of ionic groups. Another goal was to study the sulfonated polyisobutylene telechelic ionomers in nonpolar-polar solvent mixtures to determine if temperature increases cause increased viscosity as was found by Lundberg and Makowski [115] and, if so, what molecular parameters affect the temperature-viscosity relationship.

Another objective was to study the viscoelastic behavior of more concentrated solutions and gels of the sulfonated polyisobutylene telechelic ionomers in nonpolar solvents. Agarwal and Lundberg [119,120] found that concentrated solutions of sulfonated EPDM's in a nonpolar solvent display both highly viscous as well as network-like behavior depending upon the frequency of deformation and temperature. Broze et al. [122] found that concentrated solutions of the carboxy-telechelic ionomers in nonpolar solvents display a viscoelastic response which is highly dependent upon the cation used for neutralization. The unique molecular structure of the sulfonated polyisobutylene telechelic ionomers, as well as the variety of available chain microstructures, suggested that similar studies of these materials would be of interest. The goal was to characterize the influence of the various molecular parameters, such as molecular architecture, molecular weight, neutralizing cation, etc., on the viscoelastic behavior of these concentrated solutions and gels.

It was mentioned in the previous chapter that some ionomer solutions display shear thinning while some display shear thickening. The molecular factors that influence which of these two different responses occur are not clear. It was therefore considered of interest to investigate the shear rate dependent viscosity of the sulfonated polyisobutylene telechelic ionomers to hopefully shed some light on the answer to this puzzling question.

Bulk Properties of Carboxylated Elastomeric Telechelic Ionomers

Both the solution behavior and the bulk viscoelastic behavior of the carboxylated elastomeric telechelic ionomers have been studied extensively by Broze et al. [46,63,75-80,106-108]. However, the behavior of these materials at large deformations was not investigated. The typical mechanical properties, such as stress-strain behavior, ultimate properties, permanent set, hysteresis, etc., give information which is important in utilizing materials in engineering applications, as well as aiding in the determination of whether or not a particular material is suitable for such applications. Professors Robert Jérôme and Phillipe Teyssié thus requested that our research group investigate the mechanical properties of the carboxylated elastomeric telechelic ionomers to determine the influence of different molecular variables upon their behavior at large deformations.

IV. Experimental

Materials

Sulfonated Polyisobutylene Telechelic Ionomers

As mentioned earlier, the sulfonated polyisobutylene telechelic ionomers were synthesized at the University of Akron in the laboratory of Professor Joseph P. Kennedy. The syntheses were carried out by Dr. Robson F. Storey. Following the synthesis the materials were neutralized at Virginia Polytechnic Institute and State University (VPI&SU) with K^+ , Ca^{2+} , and Zn^{2+} using techniques developed by Dr. Yosef Mohajer. The author extended these same techniques to cations of valency greater than two.

Recent insight into the mechanism of carbocationic olefin polymerization has led to the synthesis of olefin telechelic polyisobutylene, i.e. PIB carrying $-CH_2-C(CH_3)_2=CH_2$ end groups. The synthesis and characterization of these linear telechelic (α,ω -difunctional) polyisobutylenes have been described previously [126-132]. The synthesis involved the use of difunctional initiator chain transfer agents known as inifers. For example, the use of the p-dicumyl chloride/ BCl_3 inifer system led to the preparation of polyisobutylenes carrying two $-CH_2-C(CH_3)_2Cl$ termini with a functionality of 2.0. Dehydrochlorination of these polyisobutylenes with a hindered base quantitatively yielded α,ω -diolefins [129]. This same concept used for the synthesis of

linear telechelics was extended to the preparation of three-arm star telechelic polymers by Kennedy et al. [126]. Similar to the synthesis of linear PIB dichlorides with the bifunctional inifer (binifer) *p*-dicumyl chloride, the three-arm star telechelic polyisobutylene trichlorides were obtained by the use of the symmetrical tricumyl chloride (TCC/ BCl_3) "trinifer" system. Subsequent quantitative dehydrochlorination of these telechelic PIB trichlorides with the hindered base *t*-BuOK under appropriate conditions led to the formation of the olefinic form of the three-arm star polyisobutylenes. Similarly, the monofunctional form of the olefinic linear PIB was synthesized using a monocumyl chloride BCl_3 "unifer" initiator. Experimental details of the synthesis and purification of these materials have been discussed by Storey [132].

Heterogeneous sulfonation was carried out in hexane solutions at room temperature. Five grams of the chloride form were dissolved in about 50 ml of hexane at room temperature. Then 1.4 ml of acetic acid were added with stirring, and after 10 minutes 0.67 ml of sulfuric acid was added. After stirring for two hours the mixture was allowed to separate and the lower sulfuric acid layer was discarded. The sulfonated product was isolated and then purified. Since the acid form is unstable at room temperature, it was then stored in a freezer until neutralized with various bases. Experimental details have been discussed by Storey [132].

The neutralization procedures developed by Mohajer have been described in detail previously [85]. The polymer acids were partially dried at room temperature under vacuum for 40 minutes and then about 2 weight percent was dissolved in a mixture of 95% hexane - 5% ethanol for neutralization with KOH. A few drops of alizarin and thymolphthalein solutions (in ethanol) were added, and the solution was titrated with an ethanolic KOH solution ($0.1 \bar{N}$) to a faint pink color. To prepare ionomers with excess neutralizing agent, the desired excess of KOH was added after reaching the endpoint. The ionomer solutions were then dried under nitrogen at about 60°C , and

then redissolved in a hexane-ethanol mixture. Then 0.2 weight percent Irganox 1010 antioxidant was added. Films were then cast and dried in a vacuum oven at 80°C for at least 24 hours. For neutralization with $\text{Ca}(\text{OH})_2$, the polymer acid was dissolved in tetrahydrofuran (THF) due to its miscibility with water - the solvent for $\text{Ca}(\text{OH})_2$. Titrations were carried out using the same indicators, and films were cast and dried as described before. Since zinc acetate is not a strong base, direct neutralization of the sulfonic acid groups cannot be carried out. Thus the required volume of $0.1\bar{N}$ aqueous zinc acetate was calculated from several titrations against a standard KOH solution. Upon addition of the zinc acetate solution, the solvent was evaporated, the ionomer was redissolved in hexane-ethanol, antioxidant was added, and films were cast and dried as before.

A similar technique was used to neutralize the polymer acids with lanthanum (III) acetate and cerium (III) acetate. Solutions were prepared by dissolving an accurately measured mass of the solid in water and diluting to the mark of a volumetric flask. Since the normalities of these solutions were known, the volume required to neutralize the polymer acid solutions could be calculated from titrations against standard KOH as before.

The sulfonated polyisobutylene telechelic ionomers were prepared in the following three molecular architectures: linear monofunctional, linear difunctional, and three-arm star trifunctional. The chemical structures are illustrated in Figure 24. The terminal sulfonic acid groups were neutralized with various bases as described above. The nomenclature used is best illustrated by an example. The designation T-14-K-0 refers to the trifunctional ionomer of $14000 \bar{M}_n$ neutralized with KOH to the endpoint (0% excess).

The neutralized materials were compression molded at 150-160°C for about 5 minutes to form films from which samples were cut. For the materials with greater than the

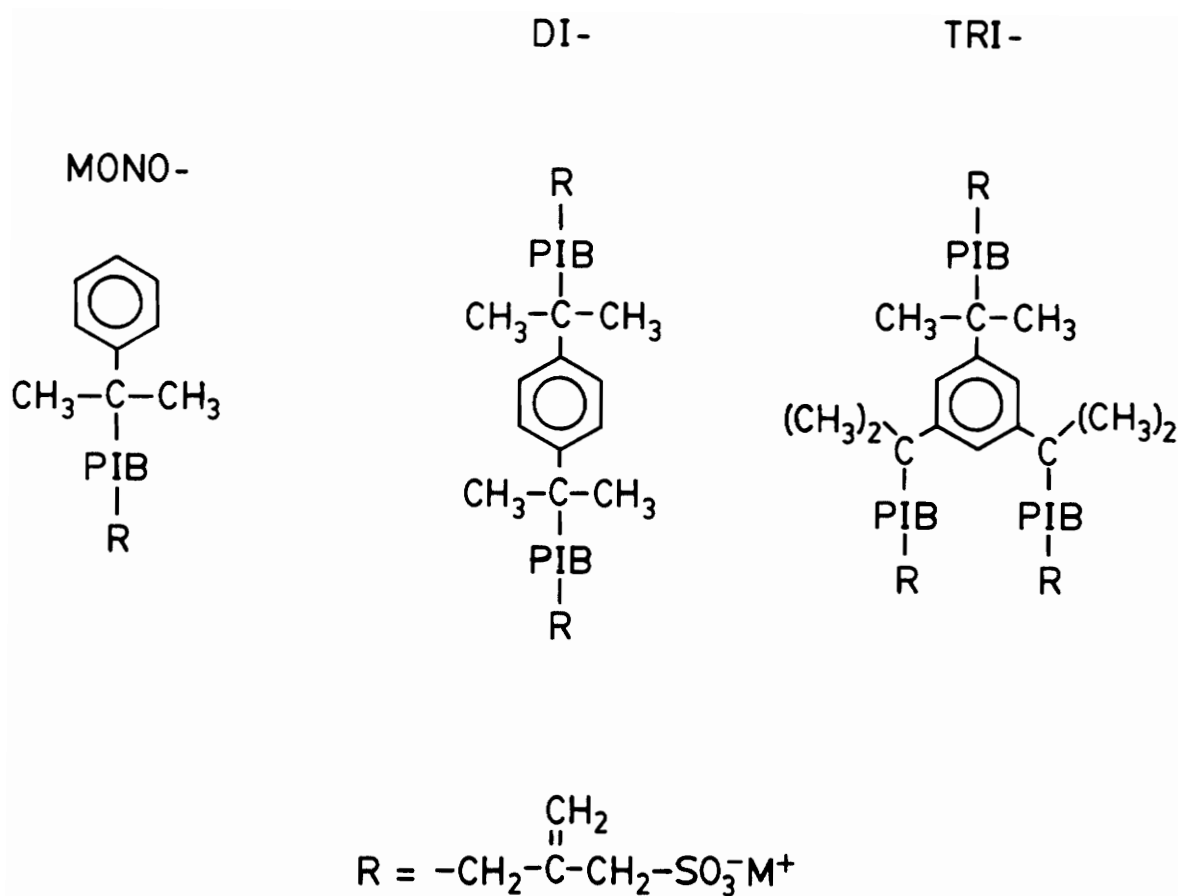


Figure 24. Chemical structures of the sulfonated polyisobutylene telechelic ionomers.

stoichiometric amount of neutralizing agent, slightly higher temperatures or slightly longer molding times were required to prepare uniform films.

Carboxylated Elastomeric Telechelic Ionomers

The carboxylated elastomeric telechelic ionomers were prepared in the laboratory of Professor Robert Jérôme of the University of Liège, Belgium. Carboxy-telechelic polyisoprene (PIP) was anionically prepared in THF at -78°C , and had a 3,4/1,2 ratio of 65/35. α -Methylstyrene sodium tetramer was used as a difunctional initiator and the living macrodianions were deactivated by anhydrous carbon dioxide [131]. Molecular weights were controlled by adjusting the monomer/catalyst ratio. Polydispersity did not exceed 1.2 and the functionality was greater than 1.95 but less than 2.0. This functionality was determined by potentiometric titration of the acid end groups with tetramethylammonium hydroxide and of the tertiary amino end groups by *p*-toluenesulfonic acid in a 9:1 benzene-methanol mixture. Amino-telechelic polybutadiene (PBD) was obtained from BFGoodrich and had an \overline{M}_n of 4000.

Carboxy-telechelic PIP was dissolved in decalin (10% w/v) and mixed with the stoichiometric amount of metal pivalate. The pivalic acid formed was removed by continuous distillation and, of course, this drove the reaction to completion. Neutralization with metal methoxides proceeded similarly in toluene instead of decalin. Further details can be obtained from Broze et al. [107]. The above syntheses and neutralizations were all conducted under strictly anhydrous conditions. In contrast, neutralizations with Group IVb metal alkoxides were conducted under nonanhydrous conditions. In fact, the introduction of water was required for the reaction to proceed. Also, a fivefold excess of the neutralizing agent was required. Broze et al. [78] suggest that the excess is needed to cap as many chain ends as possible with a carboxylato

alkoxy titanium (or zirconium). In the second step, the nonsubstituted alkoxy groups (Ti-On.Bu) carried on the prepolymer chain are progressively hydrolyzed to form Ti-O-Ti intermolecular bridges. Thus water is needed for this second step which results in the formation of crosslinks.

Experimental Methods

Small Angle X-Ray Scattering (SAXS)

Small angle X-ray scattering was used to qualitatively investigate the presence or absence of clusters in several of these ionomers. A standard Kratky small angle X-ray camera was utilized for the SAXS experiments. The X-ray source was a Siemens AG Cu 40/2 tube operated at 40 kV and 20 mA by a GE XRD-6 generator. Cu K α radiation of wavelength 1.542 Å was obtained by a Ni-foil filter. The scattered intensity was monitored by a Braun one-dimensional position sensitive detector from Innovative Technologies, Inc. In addition, some SAXS experiments were performed on selected samples by Dr. C. W. Williams using the synchrotron facility at Stanford University.

Mechanical Properties

Microbumbells 10.0 mm long were cut from the compression molded films for mechanical property studies. Stress-strain experiments were performed using an Instron Model 1122 and were conducted at room temperature at a strain rate of 100% per minute. Instantaneous set was determined by cyclic loading and unloading at the same rate to increasing strain levels in increments of 50% elongation. The end of the un-

loading cycle and the beginning of the next loading cycle was taken as the point when stress reached zero. The instantaneous set was defined as the elongation at the end of each cycle. The percent hysteresis for a given cycle was calculated as the area bounded by the loading-unloading curves to the total area under the loading curve multiplied by 100. These areas were determined using an electronic digital planimeter. Stress relaxation experiments were carried out on a Tensilon Model VTM-II (Toyo Measuring Co.) due to the excellent stability of this instrument over long periods of time. Samples were strained at a rate of 400% per minute to either 10 or 25%, and stress was monitored as a function of time. Creep experiments were conducted at room temperature by applying a load and monitoring the distance between two gauge marks. Tensile creep compliance, $D(t)$, was calculated from these data.

Dynamic Mechanical Properties

Dynamic mechanical properties were measured using a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA). The DMTA was operated in the shear mode at a frequency of 10 Hz. Scans were made from -150°C to 180°C at a scan rate of $5^{\circ}\text{C}/\text{min}$. The shear storage modulus G' and $\tan \delta$ were measured and plotted as a function of temperature. DMTA experiments were performed under a nitrogen atmosphere.

Thermomechanical Analysis

Thermomechanical analysis (TMA) was performed using a Perkin-Elmer TMS-2. The temperature range from -100°C to softening (up to 300°C) was scanned at a heating

rate of 10°C/min, and the penetration of a probe under a 10g load was monitored. TMA experiments were performed under a nitrogen atmosphere.

Solution Viscometry

Solutions were prepared in stoppered volumetric flasks using magnetic stirrers for agitation. The solvent used was either hexane or decalin (decahydronaphthalene or DHN) or a mixture of hexanol and decalin. Hexane and decalin were dried over molecular sieves. Hexanol was used as received. The kinematic viscosities were measured using calibrated Ubbelohde dilution viscometers at $25 \pm 0.1^\circ\text{C}$ in a thermostated bath. Relative viscosities (defined as η/η_s , where η is the kinematic viscosity of the solution and η_s is the kinematic viscosity of the pure solvent) were then calculated from these data. Due to the extremely wide range of viscosities encountered it was necessary to use several viscometers with different capillary sizes. In contrast to the typical procedure of calculating relative viscosity from a ratio of elution times when a single viscometer is used for both solvent and solution, absolute kinematic viscosities were first calculated and then used to calculate relative viscosities. Each data point shown in the figures represents the average of at least three experimental trials. When more than one data point is present for a particular ionomer at the same or nearly the same concentration, each data point represents results obtained from independently prepared solutions so as to check the solution preparation procedure.

Solution Viscoelasticity

Solutions were prepared by dissolving the bulk polymer in the required amount of solvent using magnetic stirrers for agitation. For very viscous solutions or gels, manual stirring was often necessary to dissolve the polymer. The nonpolar solvent used was either decalin which had been dried over molecular sieves or 100N oil, a paraffinic oil supplied through the courtesy of Dr. Pawan K. Agarwal of Exxon Research and Development Company. A Rheometrics Mechanical Spectrometer Model 605 was used in the dynamic and steady shear modes with cone (0.1 radian angle) and plate (2.5 cm diameter) geometry. A preliminary strain sweep experiment demonstrated a linear viscoelastic response at strain amplitudes up to 30%. A strain of 10% was used for the dynamic measurements. The frequency sweep covered frequencies from 10^{-1} to about 700 rad/s. The experiments were run isothermally at temperatures ranging from room temperature to 100°C.

V. Results and Discussion

Structure and Properties of Sulfonated Polyisobutylene Telechelic Ionomers in Bulk

Bulk Structure

As was discussed in Chapter III, initial SAXS studies on the sulfonated polyisobutylene telechelic ionomers did not reveal the “ionic peak” that is often observed for ionomers. Following the installation of a position sensitive detector on the SAXS apparatus in our laboratory, this work was repeated. The SAXS experiments reported here were directed at determining whether or not the sulfonated polyisobutylene telechelic ionomers display the small-angle “ionic peak”. Since this work was done at a point in time very late in this research project, and since insufficient materials were available to conduct a complete study, a thorough and quantitative analysis of the data has not been attempted.

Figure 25 shows smeared intensity vs. scattering vector for the two linear difunctional ionomers, both neutralized with 100% excess calcium acetate. The curve for the D-6.5-CaAc-100 material displays a very clear shoulder at a scattering vector of about 0.12 nm^{-1} , corresponding to a smeared Bragg spacing of about 83 Å, while the curve for the D-12-CaAc-100 material decreases monotonically with scattering angle

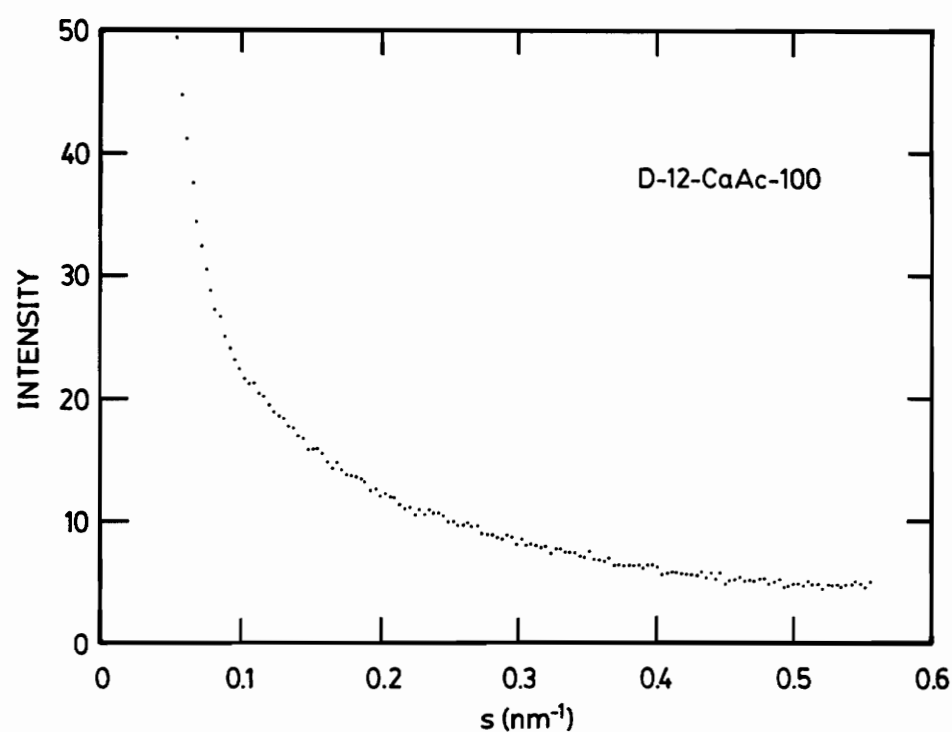
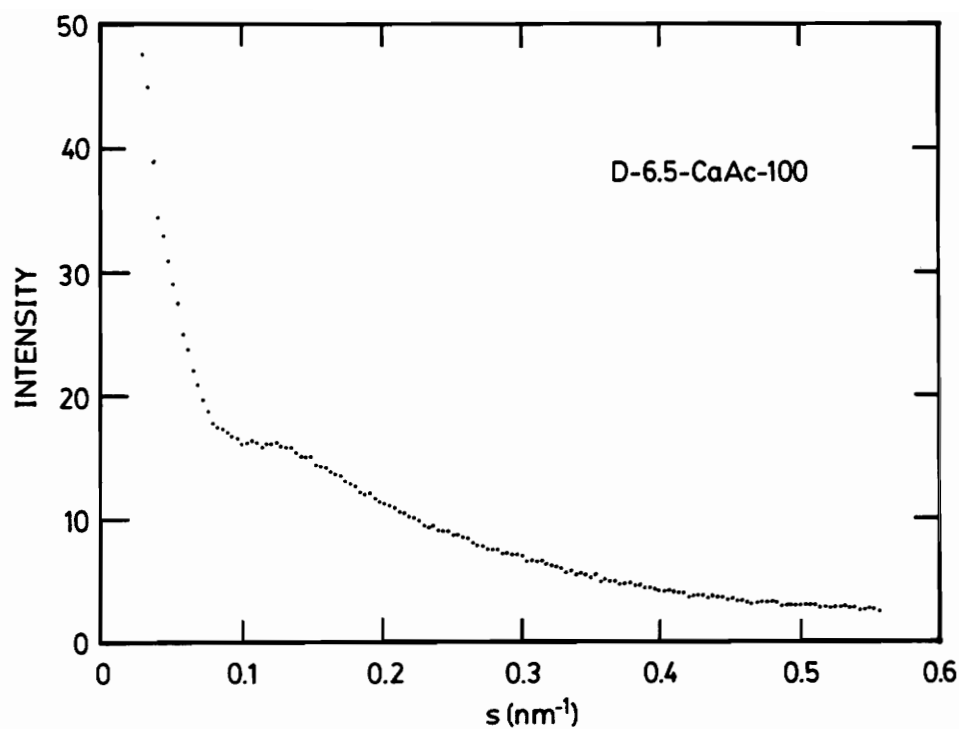


Figure 25. SAXS curves for linear difunctional ionomers: (a) D-6.5-CaAc-100 and (b) D-12-CaAc-100.

showing no indication of a shoulder. Assuming an \overline{M}_n of 6500 between ionic multiplets and using the results of calculations by Bagrodia [137] for the root-mean-square end-to-end distance of polyisobutylene one obtains about 60 Å. This is somewhat less than the Bragg spacing of 83 Å. Of course, desmearing the SAXS data would also decrease the Bragg spacing, moving it even closer to the root-mean-square end-to-end distance. Broze et al. [141] and Ledent et al. [142] have studied the SAXS behavior of carboxylated elastomeric telechelic ionomers and have found similar results, i.e. the Bragg spacing is somewhat greater than the root-mean-square end-to-end distance. As discussed in Chapter II, it is not yet clear exactly what gives rise to the SAXS peak. The lack of a shoulder for the latter material may be due to the lower concentration of ionic aggregates or it may be due to a change in the state of aggregation due to the lower concentration of ionic groups.

Figure 26 shows similar curves for two of the three-arm star trifunctional ionomers, T-8.3-K-0 and T-19-CaAc-100. Again, the curve for the lower molecular weight material, T-8.3-K-0, shows a relatively strong peak at about 0.12 nm^{-1} , while the T-19-CaAc-100 material shows a monotonic decrease in intensity with increasing scattering angle. There thus appears to be a critical molecular weight for these materials above which an ionic peak is not observed and below which the peak is observed. The \overline{M}_n between ionic multiplets should be two-thirds of the \overline{M}_n of the trifunctional molecule (8300), or 5530. Again, this is close to that of the 6500 \overline{M}_n linear difunctional species which yielded a SAXS peak at about the same Bragg spacing.

There has also been an indication that thermal history may affect the scattering behavior and thus possibly the morphological structure of the T-8.3-K-0 material. However, difficulty was encountered in reproducing this aging behavior, and a lack of sufficient material prevented the author from gaining an understanding of the phenomenon. It would certainly be desirable, after additional materials have been prepared, to

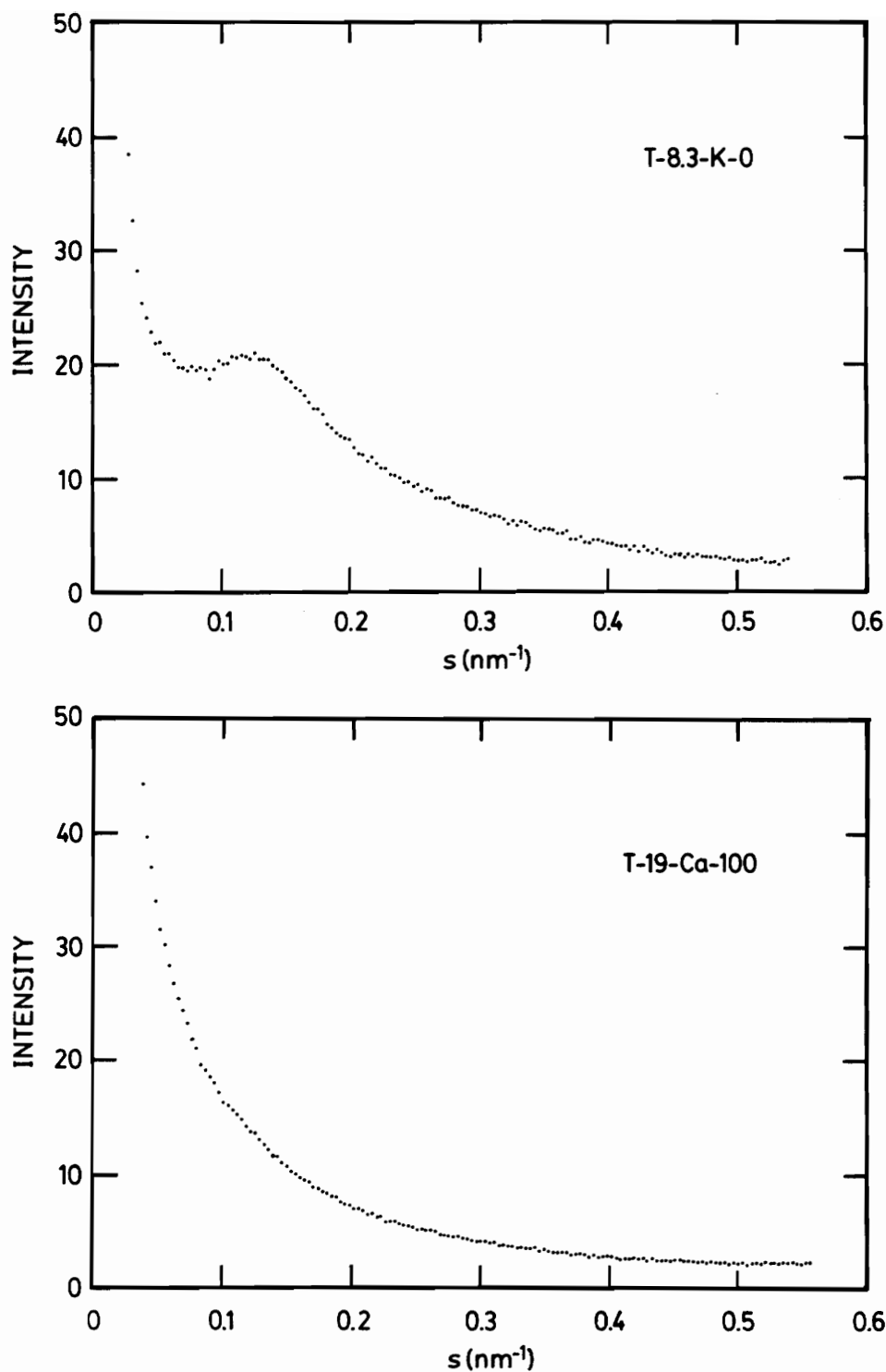


Figure 26. SAXS curves for three-arm star trifunctional ionomers: (a) T-8.3-K-0 and (b) T-19-CaAc-100.

investigate the influence of the method of preparation (e.g. solvent cast vs. thermally molded) and previous thermal history upon both the scattering behavior and the mechanical properties.

Long Term Stress Relaxation and Creep Behavior

During the course of this investigation it was found that the near equilibrium stress values reported by Bagrodia et al. [84] for stress relaxation of the three-arm star trifunctional ionomers are indeed not true equilibrium stress values. It had been reported that during stress relaxation of these materials, a near equilibrium stress is reached after about 24 hours of relaxation at room temperature. These stress relaxation experiments were conducted so that an estimate could be made of the effective crosslink density. Longer term stress relaxation experiments have revealed that this is only a plateau modulus and that substantial further relaxation occurs at longer times. However, this further relaxation does not affect the interpretation of the results of Bagrodia et al. But this further relaxation is quite important and it provides an additional means of investigating the stability of ionic networks. Figure 27 shows the effect of excess neutralizing agent upon the stress relaxation and creep behavior of the T-14-K series. In both the stress relaxation and creep data, it is clear that the material neutralized to only 90% forms a very transient network. In fact, the stress drops to about one-fiftieth of the initial stress in only 17 hours. Addition of 50% excess neutralizing agent slightly increases the initial stress, but substantially increases the stability of the network. Addition of 300% excess neutralizing agent essentially moves the stress relaxation curve to higher stresses but does not change the shape of the curve. Thus, apparently the network is strengthened but not stabilized further after the addition of 50% excess neutralizing agent. It should be noted that up to about 10^3 minutes, stress relaxation

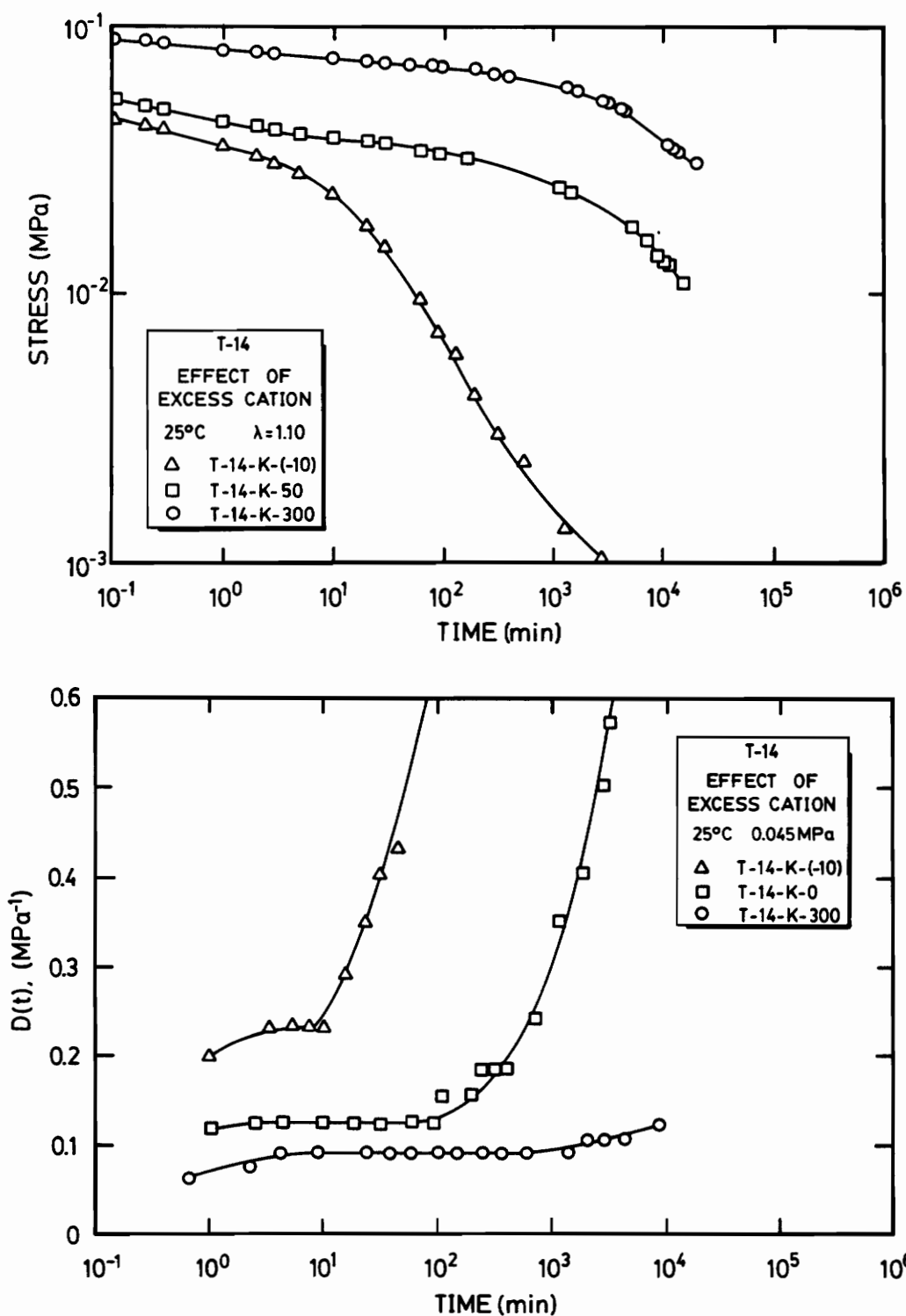


Figure 27. Stress relaxation and creep behavior of the T-14-K-X series: (a) stress relaxation and (b) creep.

progresses in an essentially linear manner on this log-log plot. Then the curve begins to turn downward and the stress relaxes more quickly with the logarithm of time. Apparently, either two different relaxation mechanisms are occurring or there is a single relaxation mechanism with a distribution that is skewed to longer times. The creep data suggest similar conclusions. Neither the under-neutralized nor the stoichiometrically neutralized materials form a network which is stable substantially beyond 1000 minutes. But the material with 300% excess neutralizing agent appears to maintain an effective network even up to 10^4 minutes. The importance of network stability in most applications is obvious, as is, therefore, the need to be able to improve or enhance it. The application of these materials should therefore be limited to those not requiring the maintenance of a stress for long periods of time.

Properties of Materials Neutralized with Elements of the Lanthanide Series

Previous studies of the sulfonated polyisobutylene telechelic ionomers have been conducted on materials neutralized with monovalent (K^+) and divalent (Ca^{2+} and Zn^{2+}) cations. It might be imagined that if the sulfonic acids could be neutralized with trivalent cations, one may be able to specifically create trifunctional ionic crosslinks. Such multifunctional crosslinks need not exist in materials neutralized with monovalent and divalent cations on the basis of electrostatic considerations alone. The goals in neutralizing the sulfonated polyisobutylene telechelic ionomers with trivalent cations were to determine how these cations might affect material properties and, specifically, to attempt to increase the strength and network stability of these materials. Figure 28 illustrates that, considering valence only and ignoring possible aggregation of ions, a divalent cation would lead to the association of only two chain ends, while a trivalent cation would form trifunctional crosslinks. In the latter case the network would, in fact,

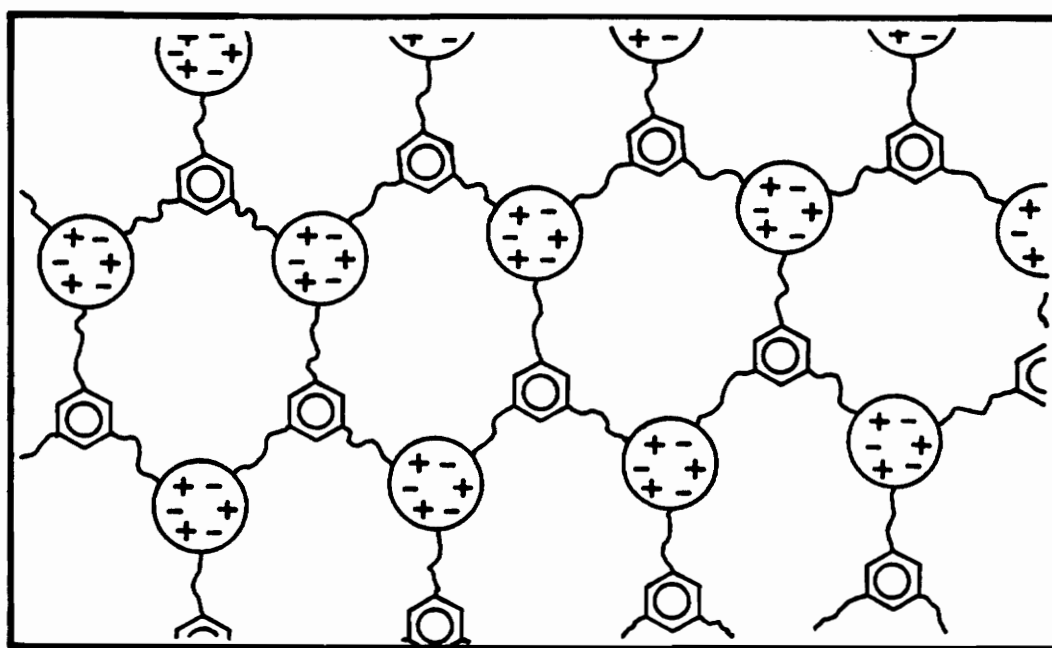
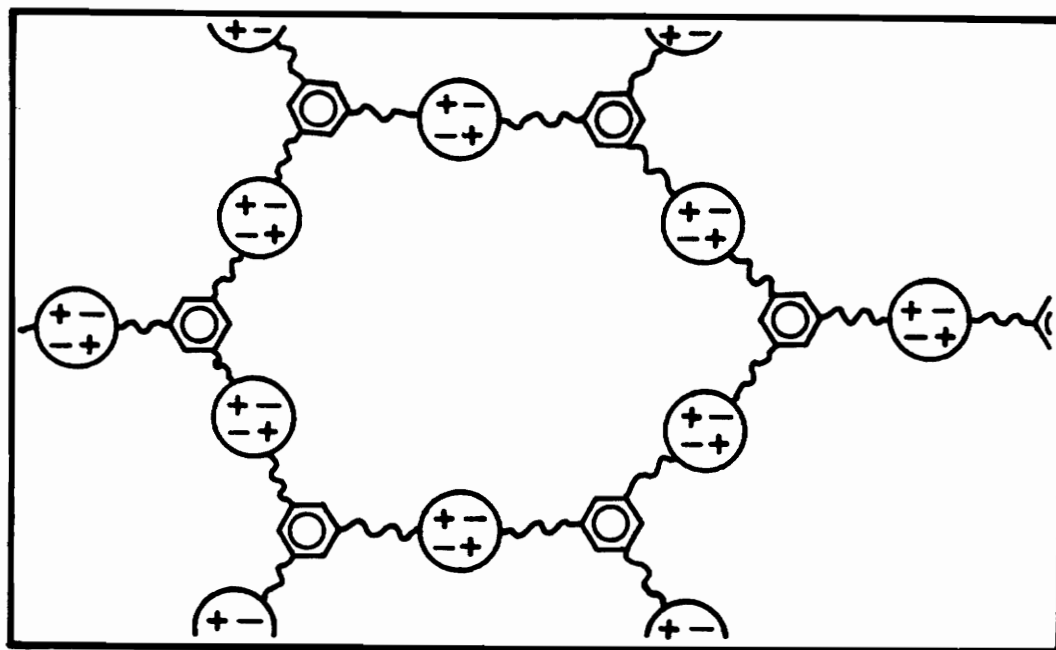


Figure 28. Comparison of networks formed by trifunctional ionomers neutralized with (a) divalent and (b) trivalent cations.: Only valence effects are considered

be an alternating covalent-ionic network and would have twice the crosslink density of the network formed by a divalent cation.

The D-6.5 material was neutralized with KOH, $\text{Ca}(\text{OH})_2$, lanthanum (III) acetate and cerium (III) acetate using the techniques described in Chapter IV. The stress-strain behavior of this series of materials (except La) is shown in Figure 29. It is clear that the behavior of the D-6.5-Ce-0 material is quite similar to that of the D-6.5-Ca-0 material, while both of these have a breaking stress which is about twice that of the D-6.5-K-0 material. Figure 30 shows the stress relaxation (except Ce) and creep behavior of these materials. It is clear from both sets of data that both D-6.5-Ce-0 and D-6.5-La-0 show enhanced network stability due to the fact that the change in relaxation mechanism appears to occur at longer times. One might get an idea of why this occurs by considering the schematic diagrams in Figure 28. Considering Figure 28a, if one sulfonate group is pulled away from the divalent cation, the other associated sulfonate group is also essentially free and becomes a dangling chain end - a network defect. On the other hand, considering Figure 28b, if one sulfonate group is pulled away from a trivalent cation, there are still two sulfonate groups attached to the cation. Thus, in this case, only one dangling chain end results while two resulted in the former case.

The T-19 material was neutralized with KOH, La(III) acetate, and Ce(III) acetate. Figure 31 shows the stress-strain behavior of these materials. Clearly, all three display the same Young's modulus, but the curves deviate from each other above 200% strain. Both the T-19-Ce-0 and T-19-La-0 materials display significantly higher stresses than the T-19-K-0 material at higher extensions, although their strain at break is somewhat lower. The stress at break is in the range of 4-5 MPa for all three materials.

Figure 32 shows instantaneous set vs. percent strain for T-19-K-0 and T-19-Ce-0. These data were obtained from the cyclic loading and unloading experiment described in Chapter IV. The instantaneous set values for T-19-Ce-0 are about 10% lower than

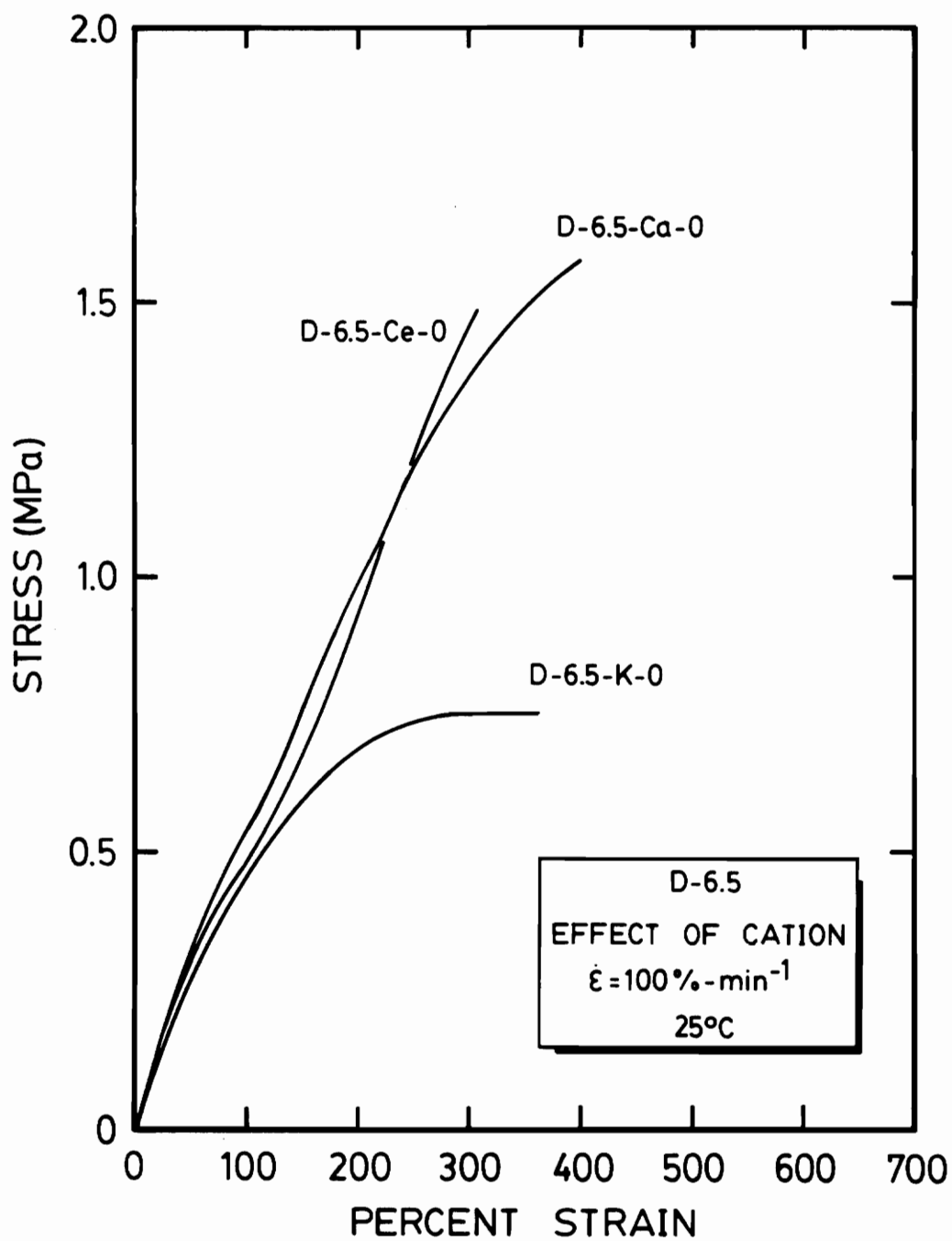


Figure 29. Stress-strain behavior of the D-6.5-X-0 series.

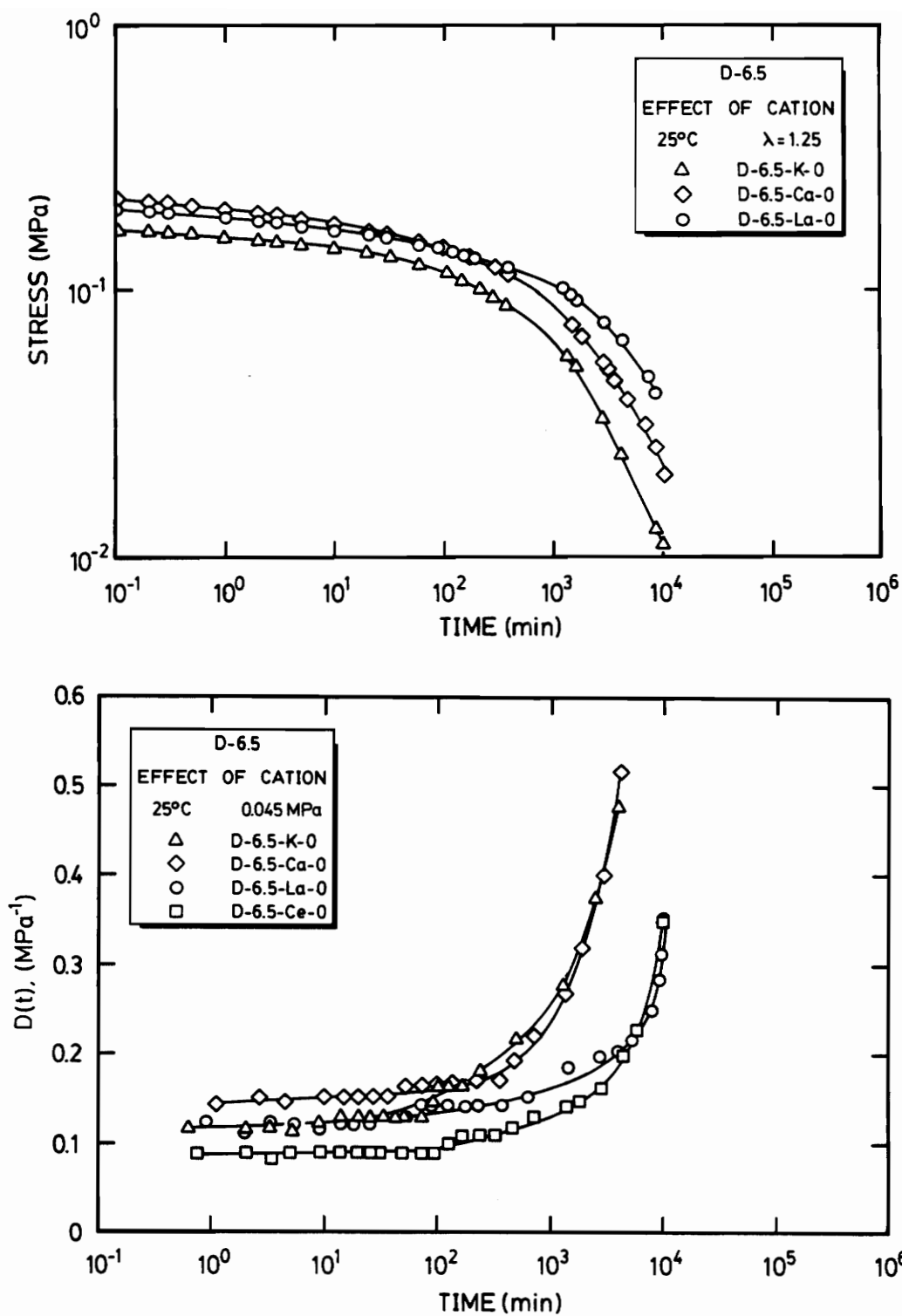


Figure 30. Stress relaxation and creep behavior of the D-6.5-X-0 series.

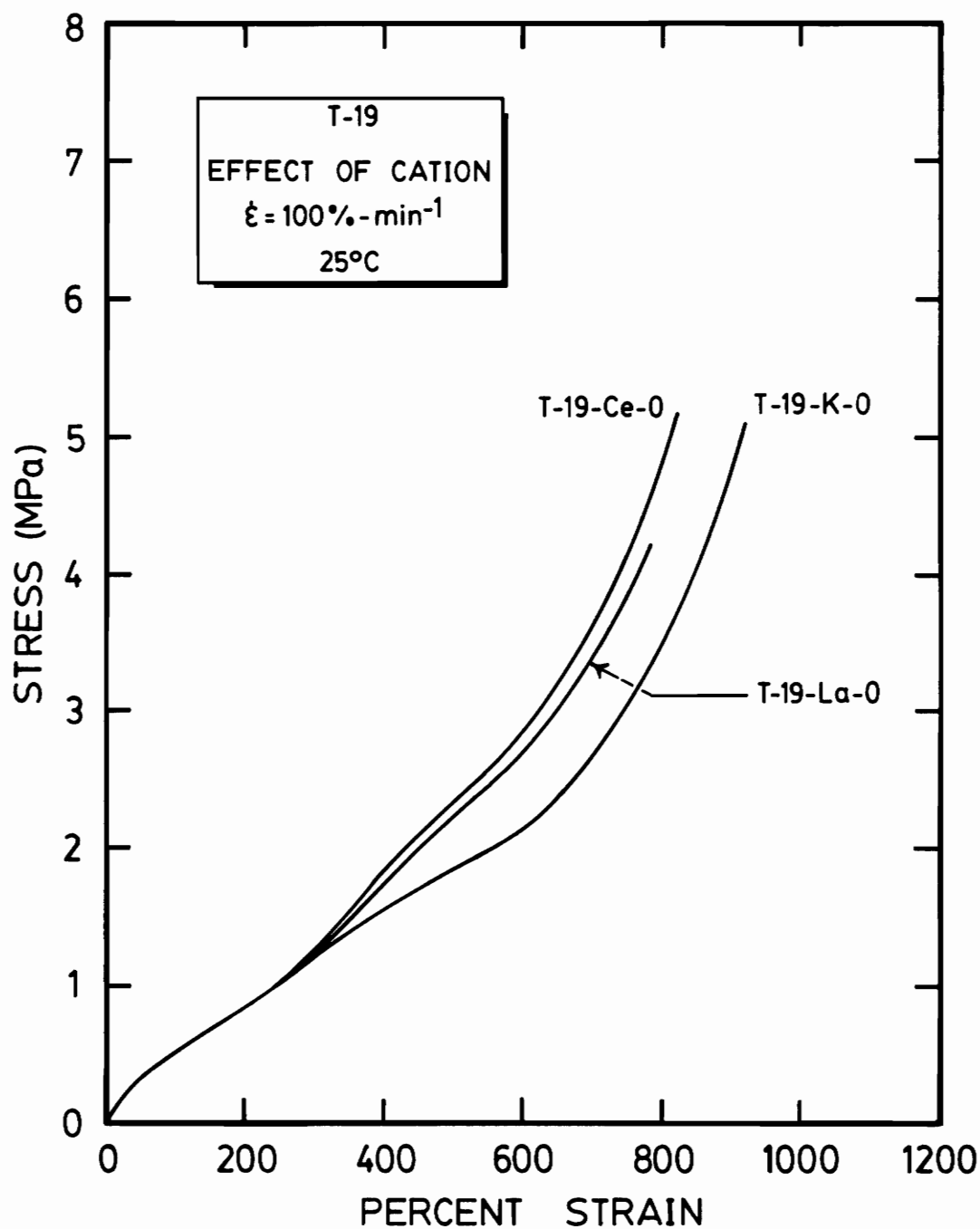


Figure 31. Stress-strain curves for the T-19 series.

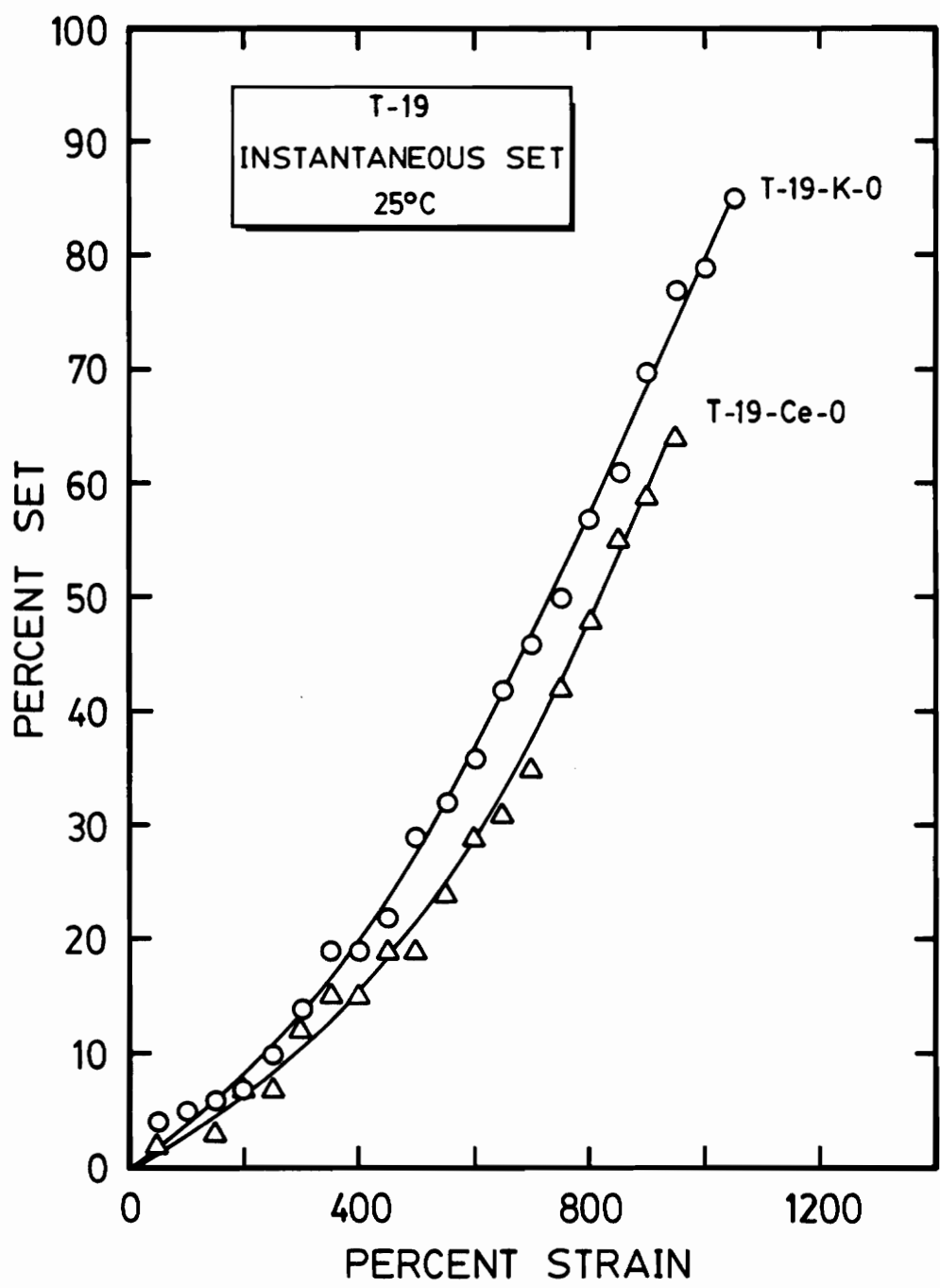


Figure 32. Instantaneous set for T-19 materials in cyclic loading-unloading experiment.

for T-19-K-0 over most of the range of percent strain, again indicating that the Ce(III) cation leads to the formation of a more stable network than does potassium.

Figure 33 shows percent set vs. recovery time for a series of T-19 samples which were maintained at 400% elongation for one week and then released. It is clear that even after 24 hours of recovery, the samples have still not reached equilibrium. What is striking about this data is that the percent set for T-19-K-0 is more than twice that for the T-19-Ca-0 and that the percent set for T-19-La-0 is only two-thirds that for the T-19-Ca-0. These data confirm that neutralization with Ca^{2+} as opposed to K^{+} results in a much more stable network and that neutralization with La^{3+} results in a network with even greater stability. The improvement in network stability when Ca^{2+} is used instead of K^{+} may be due to the fact that the ionic bonding of the two sulfonate groups is stronger than the ion-dipole association of two potassium sulfonate groups. The further stabilization provided by a trivalent cation such as La^{3+} is more likely to be due to the formation of trifunctional ionic crosslinks which increase the effective crosslink density.

Dynamic Mechanical Behavior

As discussed earlier, the fact that these materials tend to flow at elevated temperatures precludes the investigation of their dynamic mechanical properties by use of the Rheovibron. Since this instrument operates in the tensile mode with the sample oriented horizontally, gravity distorts the sample dimensions to the point where an adequate tensile force cannot be maintained. This problem is overcome in the Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) since this instrument can be operated in the shear mode, and flow of the material due to gravity is not a problem in this geometry. The primary drawback of the DMTA is that it is difficult to reproduce

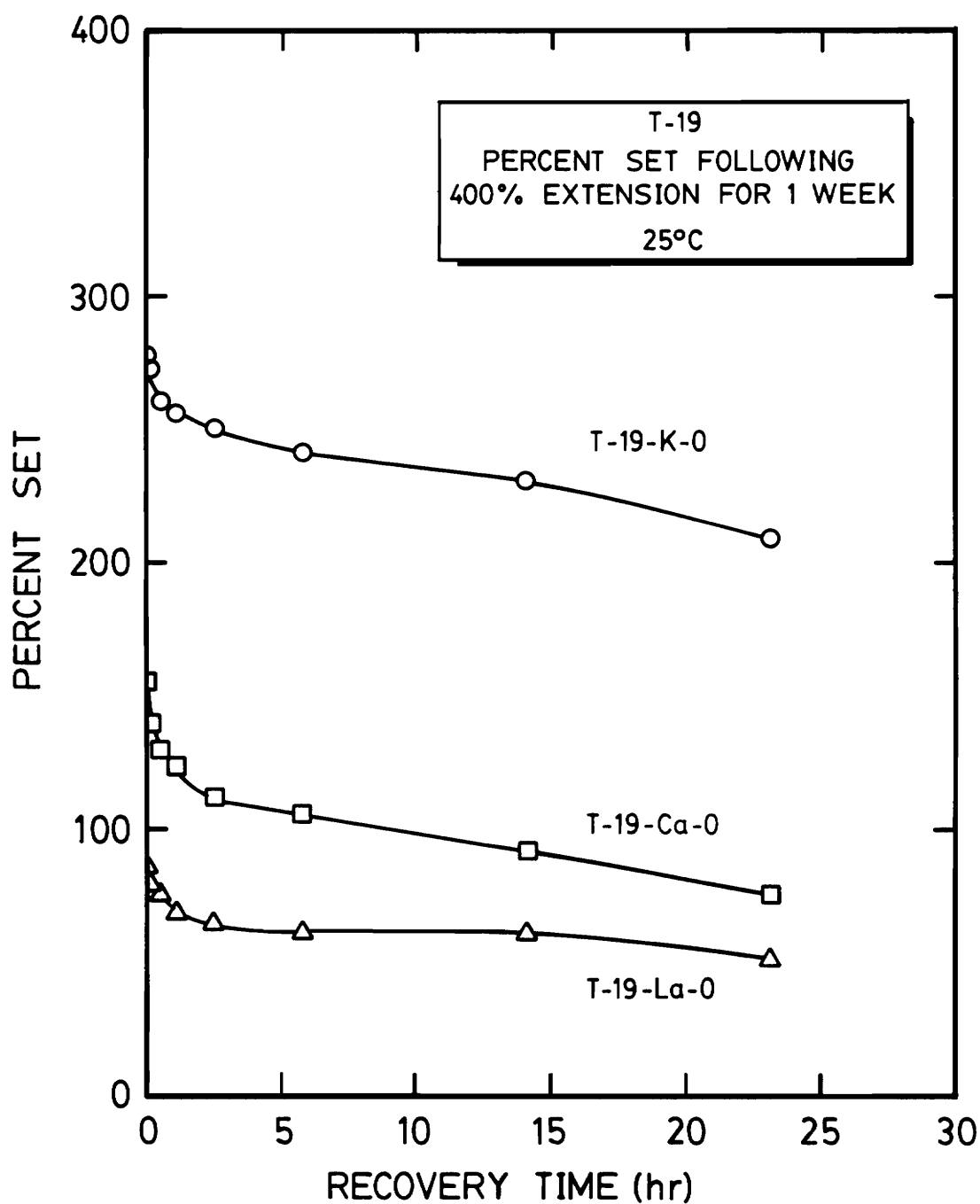


Figure 33. Recovery of T-19 materials following 400% elongation for one week.

the glassy modulus. *Therefore, in the viscoelastic data obtained on the sulfonated polyisobutylene telechelic ionomers with this instrument, the curves were shifted vertically so that the glassy modulus would be the same for all curves.* Due to this uncertainty the ordinate values of the storage modulus, G' , should therefore not be interpreted directly. Rather, the curves should be compared using the abscissa values to indicate *relative changes* in G' . This detracts somewhat from the usefulness of the data, yet, as will be seen, certain trends in the effects of system variables upon behavior can be ascertained.

Figure 34 shows the effect of molecular architecture upon the G' and $\tan \delta$ at an approximately constant \overline{M}_n of 11000-12000. The glass transition temperature is not affected by molecular architecture. The onset of the $\tan \delta$ peak here agrees with the T_g found by Bagrodia [136] by differential scanning calorimetry. The primary difference in behavior between the two materials is in the rubbery plateau region. The T-11-ZnAc-100 material displays a significantly higher modulus than the D-12-ZnAc-100 material. This is likely due to the more extensive network formed by the trifunctional material due to the fact that each molecule possesses a permanent covalent trifunctional network junction point. On the other hand, the difunctional molecules can only form a network if their terminal ionic groups form triplet or higher order associations. Such "ionic crosslinks" would be expected, of course, to be somewhat more transient in nature, thus leading to a lower modulus. The reason for the large increase in G' with temperature is not clear. Certainly the increase is much greater than that which would be expected on the basis of rubber elasticity considerations alone, i.e. a direct proportionality to temperature. One might be inclined to suggest that there may be some temperature-dependent change in the ionic associations. But, as Figure 35 shows, a similar increase in G' is observed for a linear polyisobutylene with a viscosity average molecular weight of 1.3×10^6 . Thus, too much should not be read into the magnitude of the increase in G' with temperature in the rubbery region of these

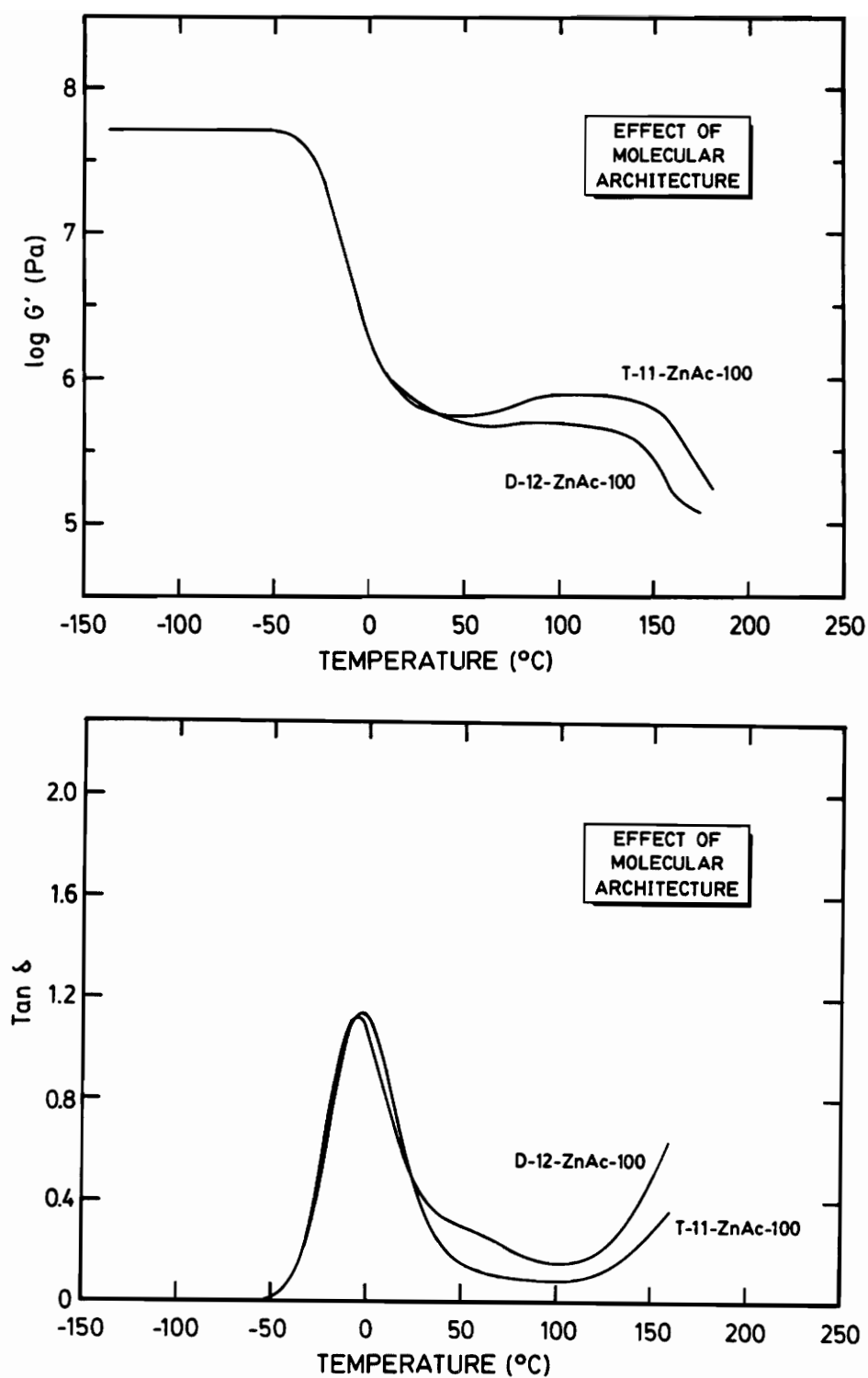


Figure 34. Effect of molecular architecture on G' and $\tan \delta$ at a relatively constant molecular weight of 11000-12000.

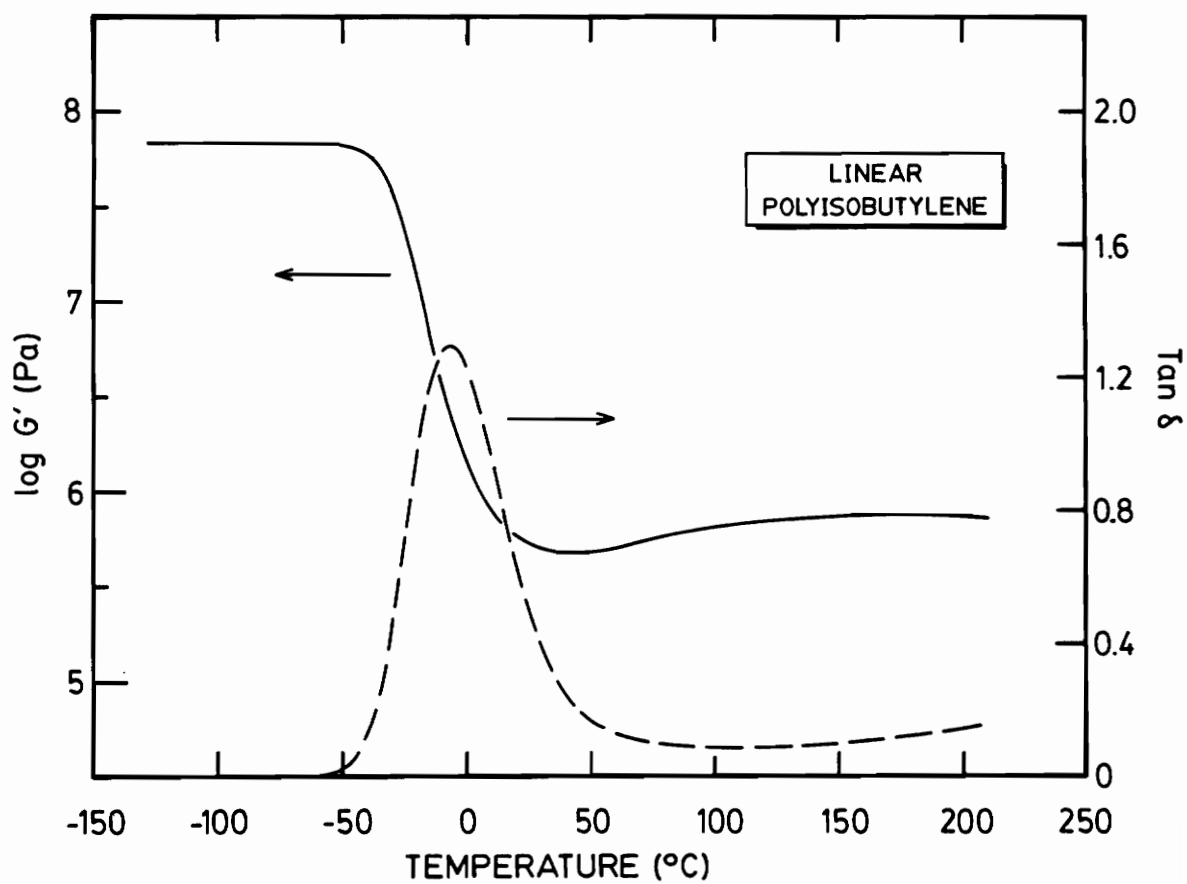


Figure 35. Dynamic mechanical behavior of linear polyisobutylene: ($\overline{M}_v = 1.3 \times 10^6$).

ionomers. Another point which should be noted is that the glass transition temperatures of the two ionomers in Figure 34 are the same as that of the high molecular weight linear polyisobutylene shown in Figure 35. Even the breadth of the transition region is essentially the same. Thus the glass transition is apparently not affected by the presence of ionic groups.

Figure 36 shows the effect of molecular weight upon G' and $\tan \delta$ for the T-X-K-100 material. Considering only the G' data, it might be suggested that T_g is affected by molecular weight. However, this is likely due to the vertical shifting procedure employed since the $\tan \delta$ data indicate that T_g is not affected by molecular weight. As \overline{M}_n increases from 8300 to 11000 to 19000, G' in the rubbery plateau region decreases due to the decreasing effective crosslink density. However, upon increasing the molecular weight to 34000, a large increase in the plateau modulus is observed. This is quite similar to the behavior of the linear carboxy-telechelic ionomers studied by Jerome and Broze [80] as shown in Figure 9 on page 35. These workers suggest that at low molecular weights the ionic crosslink density is the parameter which controls G' . Thus, as molecular weight increases the ionic crosslink density decreases, resulting in a decrease in G' . However, a certain critical molecular weight is reached where physical entanglements begin to dominate the response and G' therefore begins to increase again.

Figure 37 shows the effect of cation type upon the G' and $\tan \delta$ of the D-6.5 material. All of the cations are present in stoichiometric amounts except for the zinc-neutralized material which has 100% excess. Even with this excess the zinc-neutralized material has a less well developed rubbery plateau and flow is observed at a much lower temperature than for the materials neutralized with other cations. It is also observed that the T_g of the zinc material is slightly lower than for the other materials. The materials neutralized with K^+ , Ca^{2+} , La^{3+} , and Ce^{3+} behave similarly with the rubbery modulus decreasing in the order $K^+ > Ce^{3+} = La^{3+} > Ca$. Although it is easy to

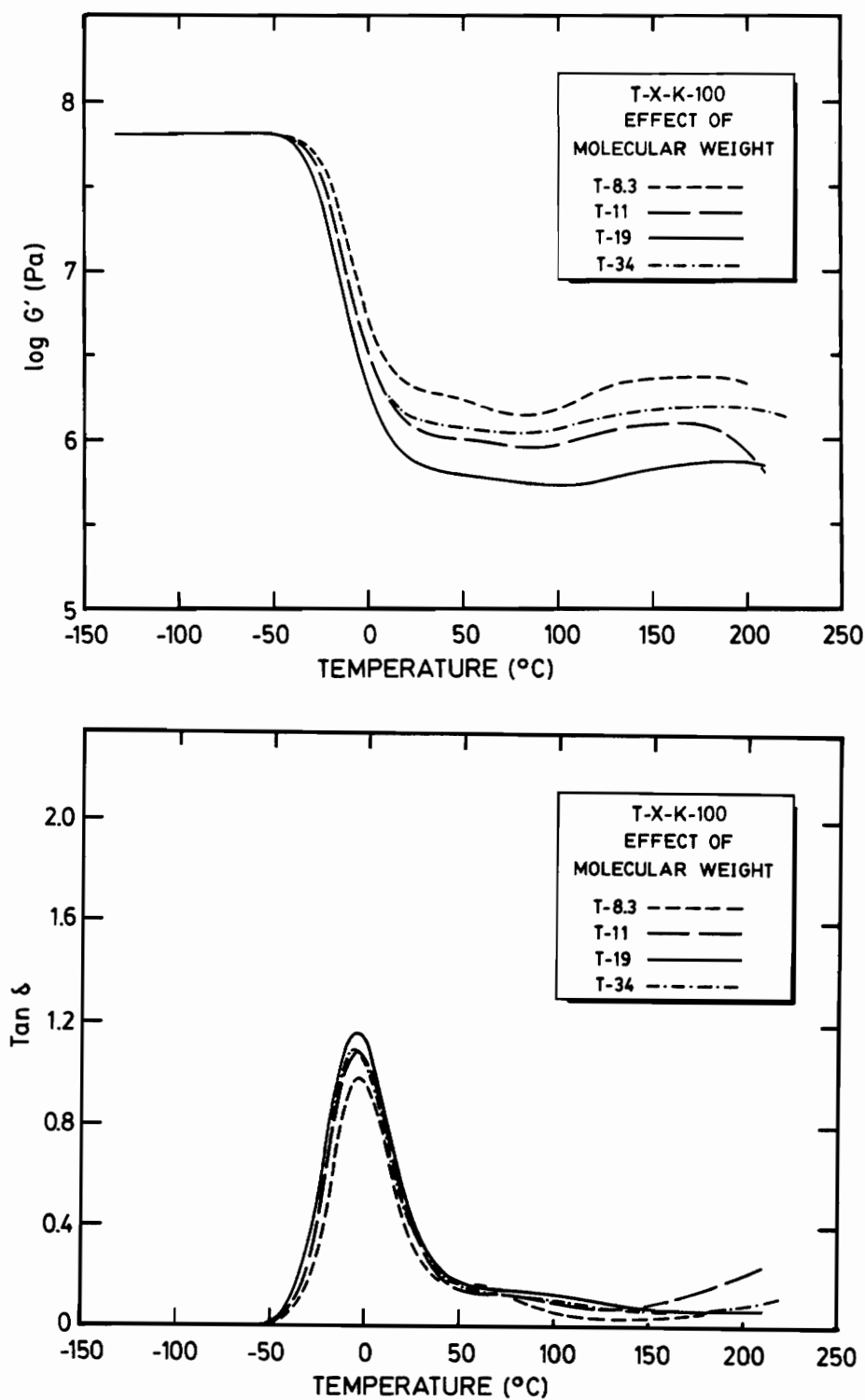


Figure 36. Effect of molecular weight on G' and $\tan \delta$ of trifunctional ionomer.

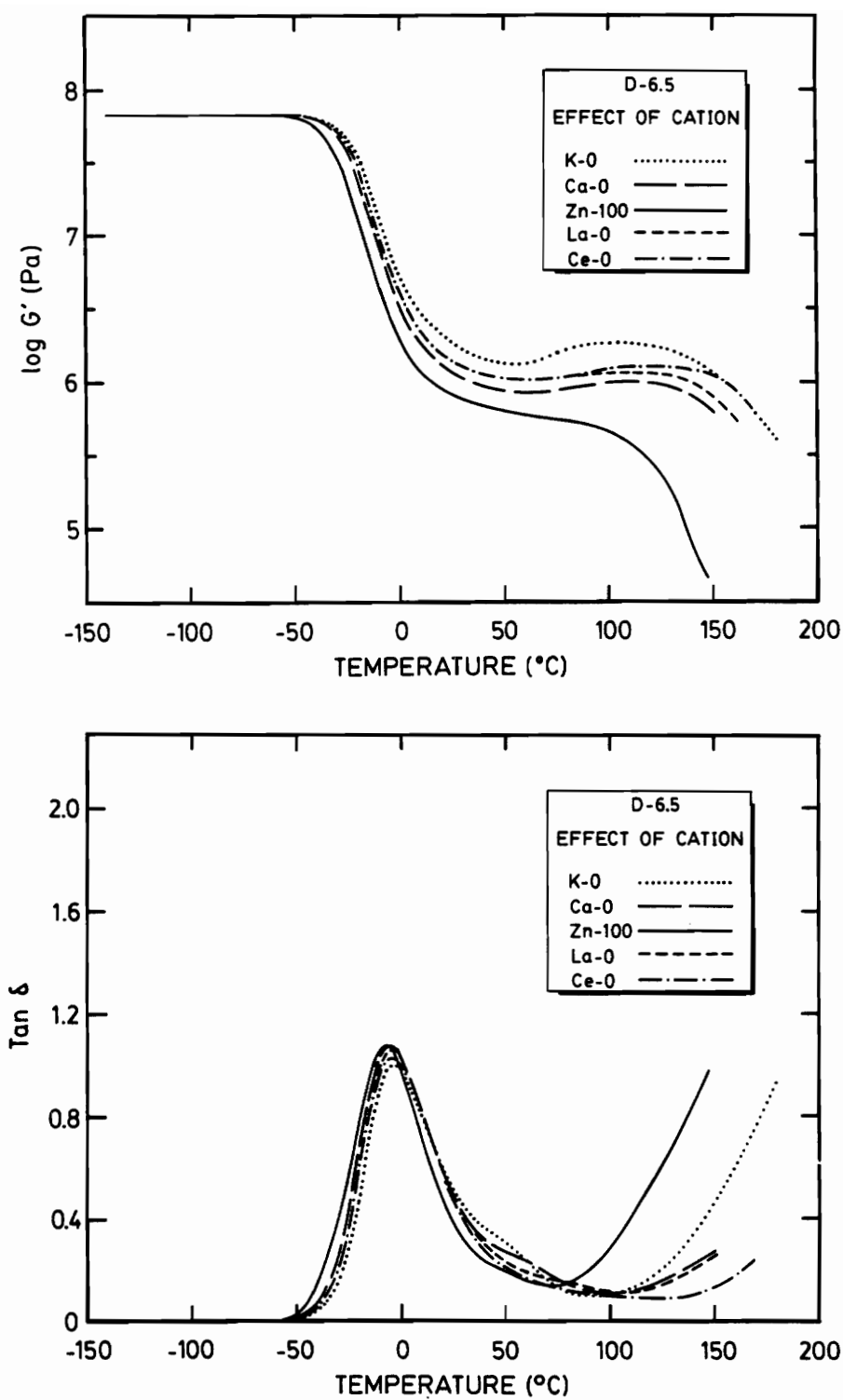


Figure 37. Effect of cation type on G' and $\tan \delta$ for the D-6.5 series.

understand why the plateau moduli of the Ce^{3+} and La^{3+} materials are about the same and are slightly higher than that for the Ca^{2+} material, the reason for the G' of the K^+ material being significantly higher is not clear. The $\tan \delta$ data indicate the order in which flow appears to begin. The zinc material begins to flow at the lowest temperature followed by K^+ , Ca^{2+} , La^{3+} , and Ce^{3+} .

Figure 38 shows the effect of excess cation on the T-14-K series. Except for the under-neutralized material, T-14-K-(-10), all of the materials display similar rubbery plateaus. T-14-K-(-10) begins to flow at a much lower temperature than the others, as would be expected, followed by T-14-K-0. The three materials with excess neutralizing agent all begin to flow at about the same temperature. This result is somewhat different than that observed by Bagrodia et al. [86] based on thermomechanical measurements. The likely explanation is that the data presented here are dynamic data while the thermomechanical data were obtained by maintaining a constant stress on the sample while scanning temperature. Ionic associations are likely to be maintained at higher temperatures unless an adequate stress is applied to disrupt them. Again, the $\tan \delta$ data indicate that T_g is unaffected by excess neutralizing agent.

Summary

These studies of the bulk properties of sulfonated polyisobutylene telechelic ionomers have resulted in several important findings. First, low molecular weight ionomers ($< 10,000 \overline{M}_n$) display an “ionic peak” or at least a shoulder in the scattering curve. At higher molecular weight (lower ionic concentration) such a peak is not observed. Second, at very long times ($> 10^4$ minutes) the stress relaxation mechanism changes, resulting in a more rapid relaxation with the logarithm of time. The materials are observed to flow due to the breaking and reforming of the ionic associations. Third,

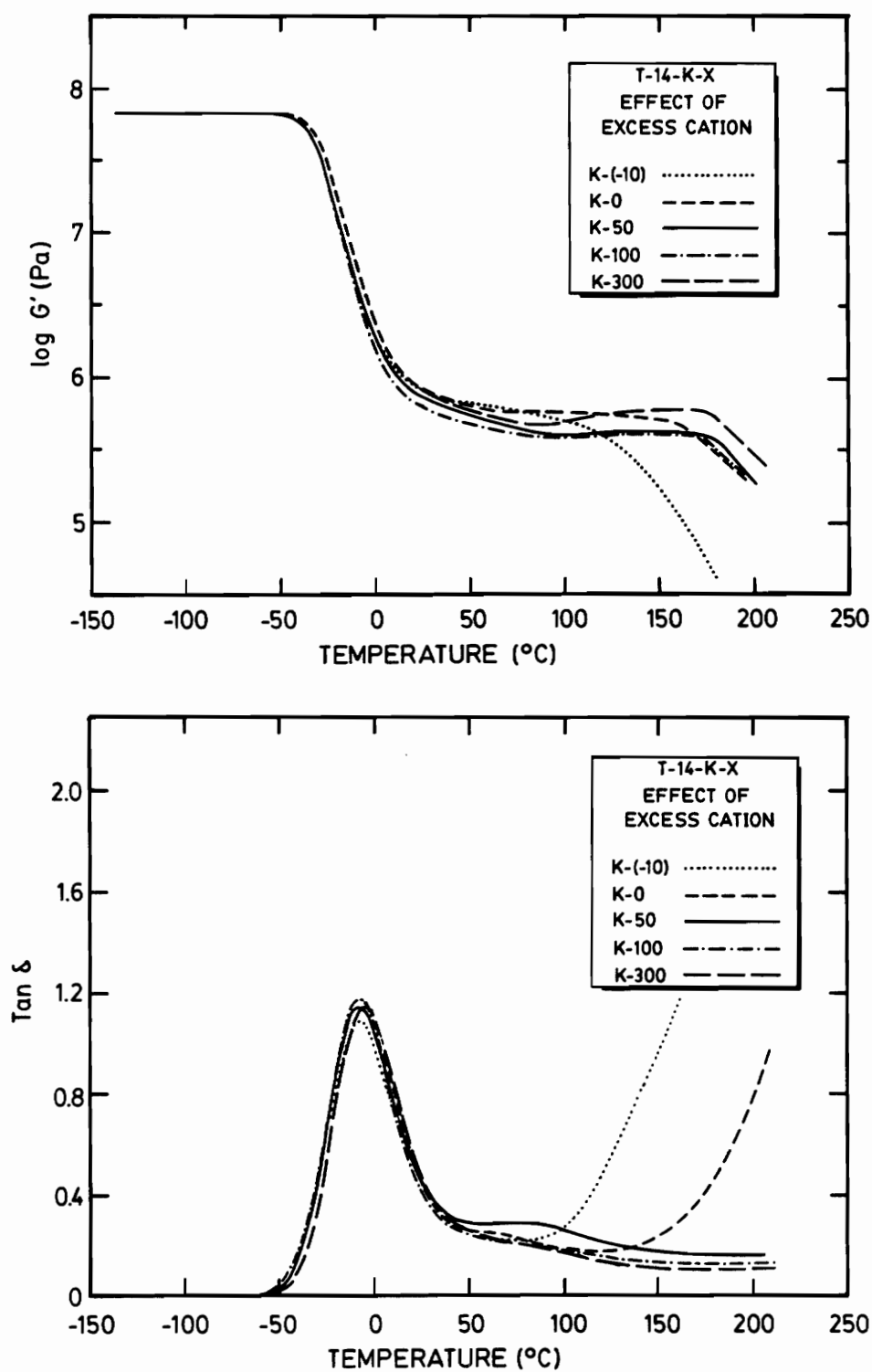


Figure 38. Effect of excess cation on G' and $\tan \delta$ of T-14-K series.

neutralization with trivalent cations such as Ce^{3+} and La^{3+} result in networks which are more stable than those formed by K^{+} and Ca^{2+} cations. This is likely due to the higher ionic crosslink density resulting from neutralization with trivalent cations.

Viscometric and Viscoelastic Behavior of Sulfonated Polyisobutylene

Telechelic Ionomers in Solution

The primary goals of the solution work conducted on the sulfonated polyisobutylene telechelic ionomers were (1) to learn about how ionic interactions are affected by solvent environment, (2) to determine the effects of molecular variables such as architecture, molecular weight, neutralizing cation, etc., and (3) to provide data which might be useful in determining exactly how these materials could be used as viscosity control agents. The viscosity behavior was studied in both nonpolar solvents and nonpolar-polar solvent mixtures. The viscoelastic behavior of concentrated solutions in nonpolar solvents was also studied to learn more about the dynamic nature of these ionic interactions.

Viscometric Behavior of Dilute Solutions

Nonpolar Solvents

The advantage to studying the behavior of ionomers in nonpolar solvents is that nonionic intermolecular interactions (segment-segment, entanglements, etc.) are reduced while maintaining the level of ionic interactions. Thus the effects of the ionic parameters on the strength of ionic association may be elucidated more clearly.

The studies by Broze et al. [106-108] on the gelation of the carboxylated elastomeric telechelic ionomers in nonpolar solvents was discussed earlier (see Figures 17 and 18 on pages 55 and 57]. Similar studies were conducted on the sulfonated polyisobutylene telechelic ionomers to determine how the various molecular variables affect the gelation concentration in a nonpolar solvent.

The nonpolar solvent used in this work was hexane. Figure 39 shows the effect of sulfonation and neutralization upon the relative viscosity vs. temperature behavior for the linear difunctional ionomer of 12000 \overline{M}_n which was neutralized to the endpoint with KOH (i.e. D-12-K-0). The linear increase in the logarithm of relative viscosity as a function of concentration for D-12-HC (the hydrocarbon form prior to sulfonation) is typical of low molecular weight polymers in this concentration range. The nonlinear increase in the logarithm of relative viscosity for D-12-SO₃H indicates some association of the ionic groups. Such association was not observed for the carboxylated linear telechelic polymers of Broze et al. [106,107], for which the logarithm of viscosity continued to increase linearly for the acid form at these concentrations. This difference is another indication that sulfonic acid groups associate more strongly than carboxylic acid groups. A high degree of association for the sulfonic acid form of these PIB-based ionomers was also previously observed in the bulk material [86]. These associations are not maintained at room temperature due to decomposition of the sulfonic acid terminal groups, and viscosity is observed to decrease with time. The data shown were obtained as quickly as possible following dissolution of the polymer. Neutralization of the sulfonic acid groups with KOH greatly strengthens the ionic associations as shown in Figure 39. The gelation observed for D-12-K-0 is similar to that observed by Broze et al. [106-107] for linear telechelic polymers (polybutadiene, polyisoprene, poly(α -methylstyrene) etc.) with neutralized carboxylic acid groups. Sulfonation and neutralization have a similar effect upon the viscosity behavior of the trifunctional

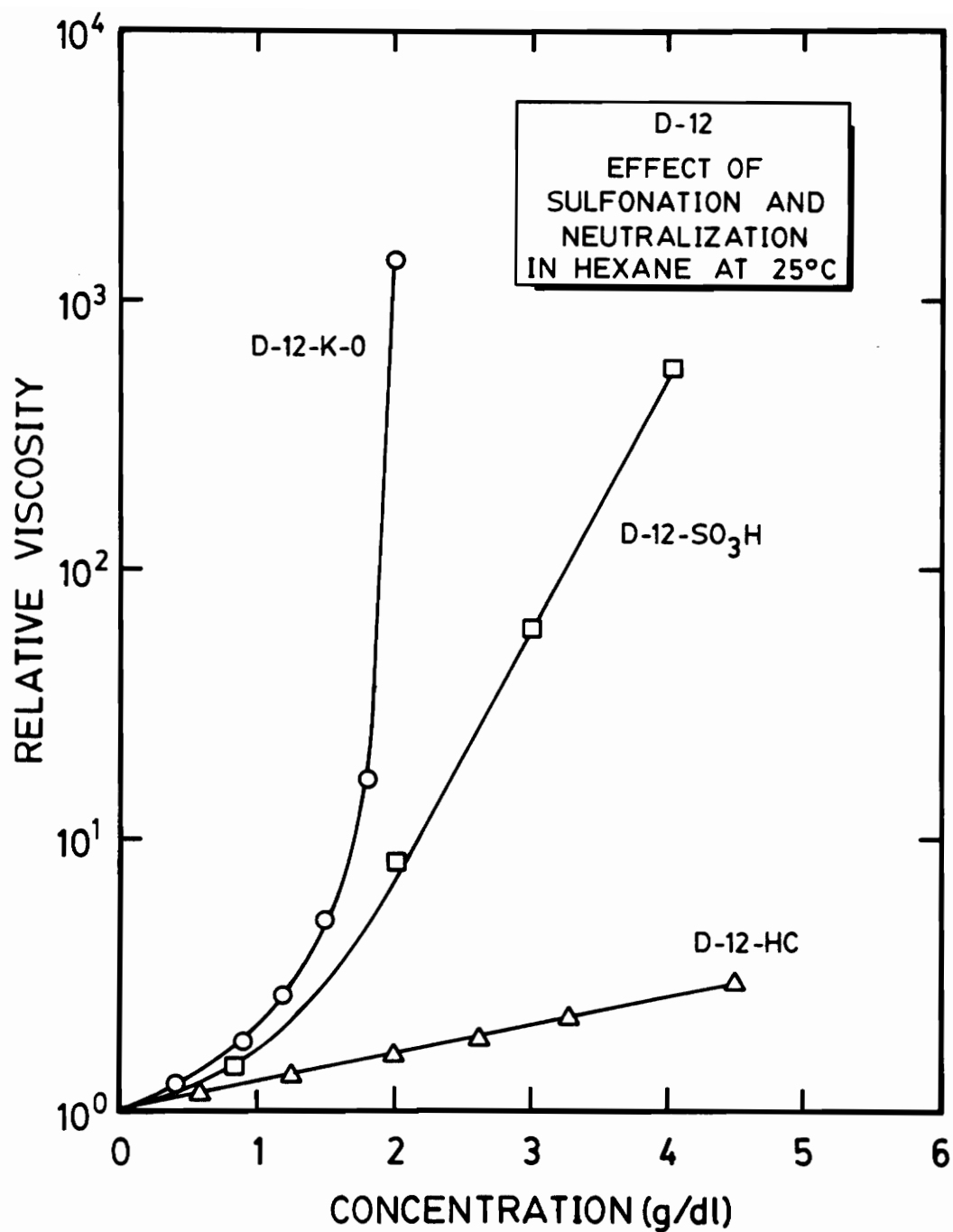


Figure 39. Effect of sulfonation and KOH neutralization upon relative viscosity for D-12-K-0 in hexane.

ionomer as shown in Figure 40 for the 14000 \overline{M}_n polymer. It should be noted that following dissolution of the neutralized ionomers, viscosity measurements were made at various times up to two weeks after solution preparation. Viscosities were found to be stable over this period of time.

The gelation of telechelic polymers in a nonpolar solvent results from association of the ionic endgroups. If triplet or higher order associations are possible, as suggested by Broze et al. [106-108], then linear telechelic polymers may indeed form a network in solution. Intermolecular ion pair association would result in simple chain extension and an increase in viscosity due to the increase in apparent molecular weight. However, it seems difficult to attribute increases in viscosity of several orders of magnitude to simple chain extension. Assuming that only chain extension occurs, it is possible to calculate the apparent degree of polymerization, \overline{DP} , as a function of concentration from the relative viscosity. In other words, the apparent \overline{DP} is that \overline{DP} which would be necessary to cause the observed relative viscosity. The specific viscosity, η_{sp} , is given as a function of the intrinsic viscosity, $[\eta]$ by the equation

$$\eta_{sp} = [\eta] + k_1[\eta]^2c \quad (5.1)$$

which is known as the Huggins equation [137]. The specific viscosity is given by

$$\eta_{sp} = \eta_{rel} - 1 \quad (5.2)$$

and the intrinsic viscosity by

$$[\eta] = \frac{\eta_{sp}}{c} \Big|_{c \rightarrow 0} \quad (5.3)$$

The intrinsic viscosity is also related to the viscosity-average molecular weight, \overline{M}_v , by the empirical Mark-Houwink equation, i.e.

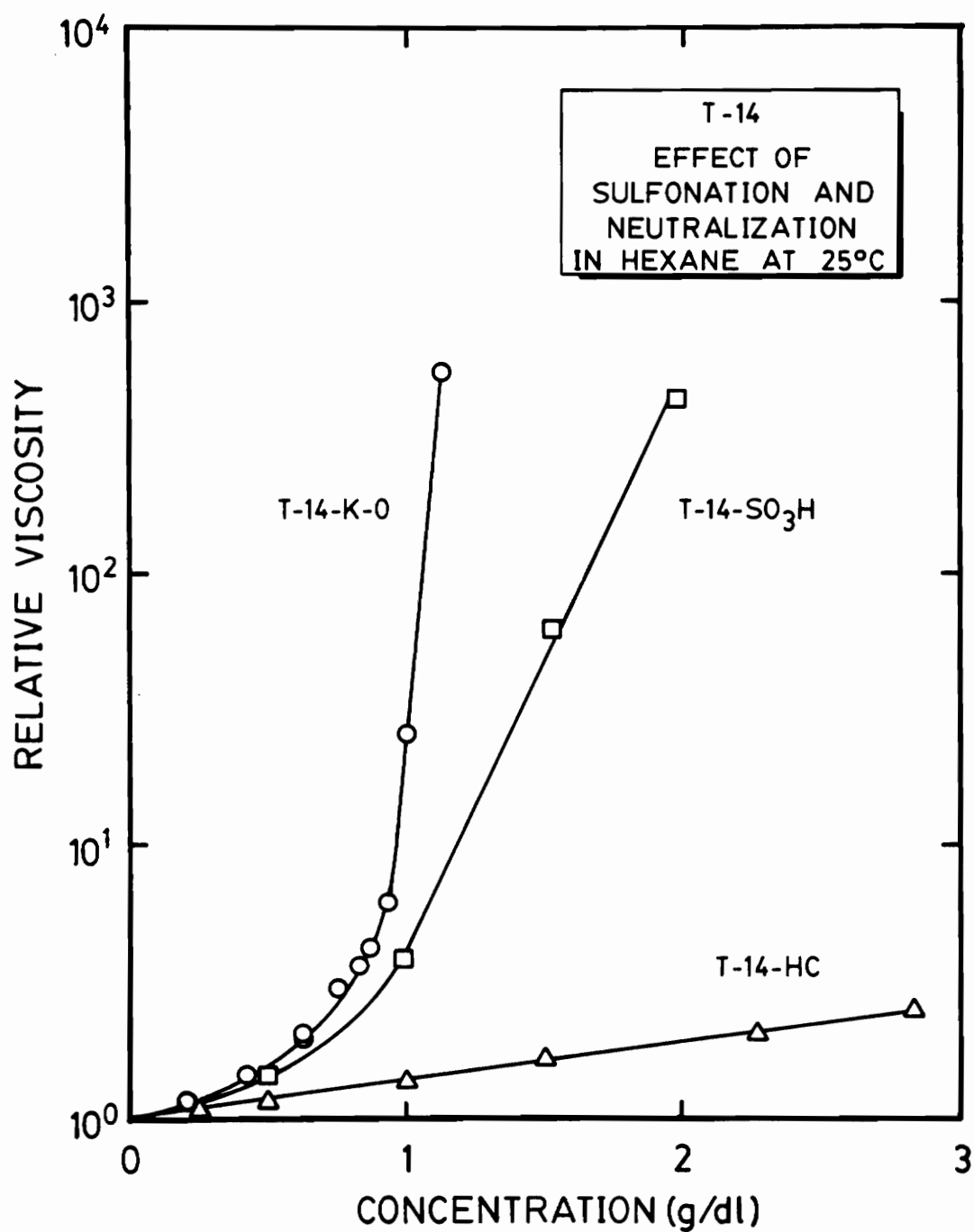


Figure 40. Effect of sulfonation and KOH neutralization upon relative viscosity for T-11-K-0 in hexane.

$$[\eta] = k\overline{M}_v^a \quad (5.4)$$

where k and a are constants dependent upon the polymer-solvent system. Substituting equation (5.4) into equation (5.1) gives

$$\frac{\eta_{sp}}{c} = k\overline{M}_v^a + k_1k^2\overline{M}_v^{2a}c \quad (5.5)$$

Assuming that only chain extension occurs, the apparent \overline{M}_v may be calculated at various concentrations since η_{sp}/c is measured directly and $a = 0.7, k = 2.6 \times 10^{-4}$, and $k_1 = 0.3$ for the polyisobutylene-hexane system [137]. The apparent degree of polymerization, \overline{DP} , is then calculated by dividing the apparent \overline{M}_v by \overline{M}_n . Of course, this calculation is accurate only for a narrow molecular weight distribution and becomes exact for a polydispersity of 1.0. For these ionomers $\overline{M}_w/\overline{M}_n = 1.7$ and therefore the calculation is an approximation. The results for D-6.5-K-0 and D-12-K-0 are shown in Figure 41. It is certainly not clear why there should be an abrupt increase in the apparent degree of polymerization below 2 g/dl, which would occur if chain extension was solely responsible for the viscosity increase. It is likely that the ionic associations that occur are of both types, i.e. triplets and higher order associations which result in multifunctional network junction points and ion pair associations which result in simple chain extension. Dynamic experiments on gels formed by these linear difunctional materials, and which will be discussed later, suggest that an elastomeric network is indeed formed since the storage modulus G' is in some cases constant over the entire range of experimentally accessible frequencies. Intramolecular ion pair associations may also occur, resulting in cyclic structures. These cyclic species may be mutually independent or they may be interlocked to form catenates as suggested by Broze et al. [108]. Figure 42 contrasts the results of intermolecular association (chain extension) vs. intramolecular

association (cyclic formation). Recently, Misra and Mandal [108] have suggested, based upon osmotic pressure measurements, that the degree of association remains essentially constant in the concentration range where gelation occurs. These workers assert that a high degree of association exists even at very low concentrations and that this should be reflected in an abnormally large Huggins coefficient.

The effect of molecular architecture upon the relative viscosity is shown in Figure 43 where architecture is varied while holding molecular weight approximately constant. The solution of M-11-K-0 does not gel even at higher concentrations since ion pair association would lead only to dimerization. In fact, ionic associations which involve three or more ion pairs would result in the formation of star-like molecules or micellar structures with a central ionic region. The slight downward curvature of the relative viscosity vs. concentration plot for M-11-K-0 may indicate that as concentration is increased the average number of arms per star increases. The probability of triplets and higher order associations should increase with increasing concentration. Once a few arms are present, however, the addition of more arms of common length has very little effect on the radius of gyration [133,135]. Therefore, as the concentration of the linear monofunctional ionomer is increased, the viscosity increases due to the presence of more polymer; however, it does not increase linearly since some of the added molecules are incorporated into stars which already exist and to which they contribute very little additional hydrodynamic volume. (The ultimate number of arms per star would be limited by steric considerations.) The viscosity vs. concentration curve would then be expected to exhibit a decreased rate of viscosity increase as observed. As shown in both Figures 39 and 43, the solution of D-12-K-0 does display gelation. The solution of T-11-K-0 also gels but at a much lower concentration than the D-12-K-0. This behavior most likely occurs for two reasons. First, the number of ionic groups per molecule is greater for the trifunctional ionomer, so that for molecules of the same molecular weight the ionic

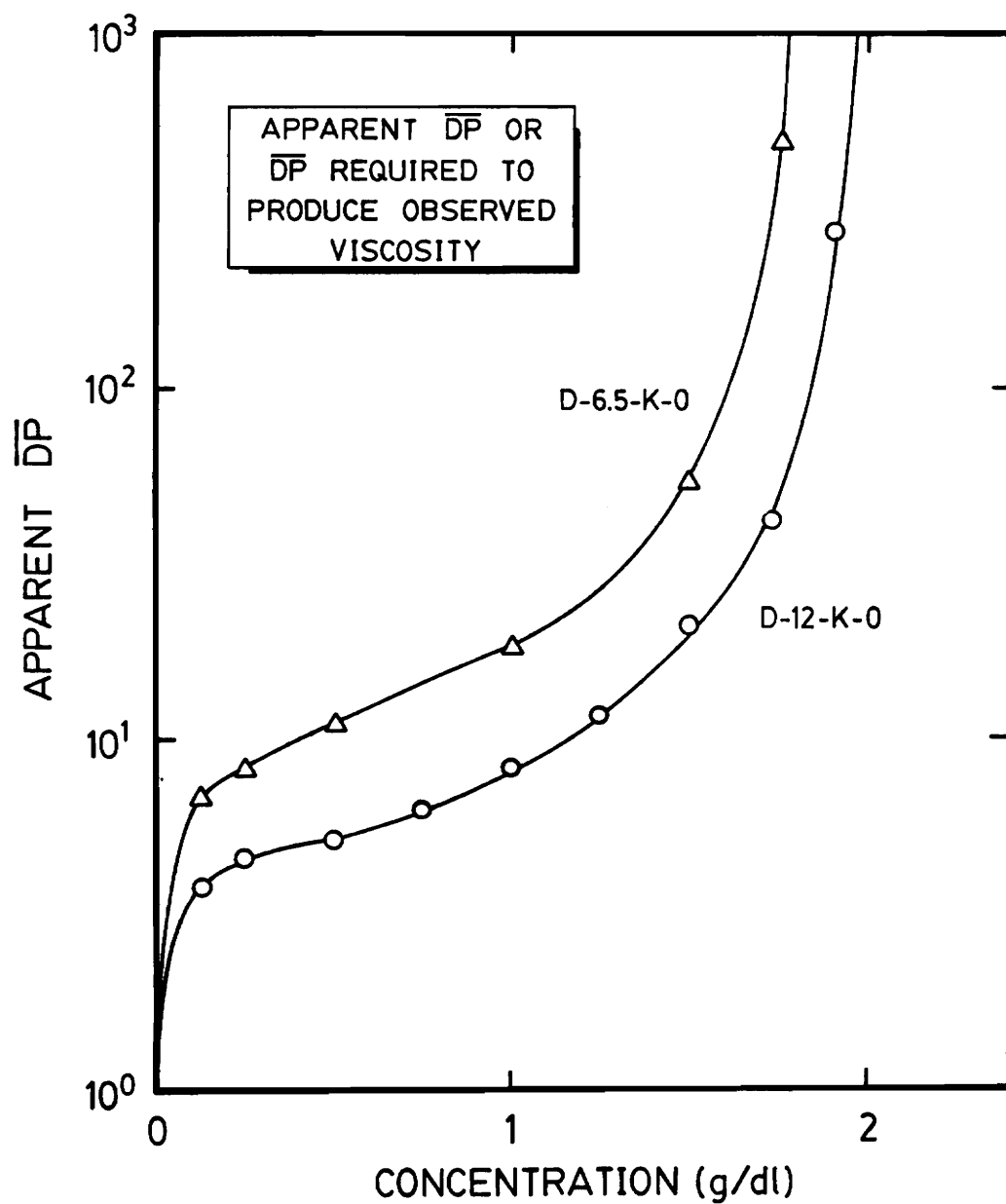


Figure 41. Apparent degree of polymerization required to produce observed viscosity for D-6.5-K-0 and D-12-K-0 in hexane.

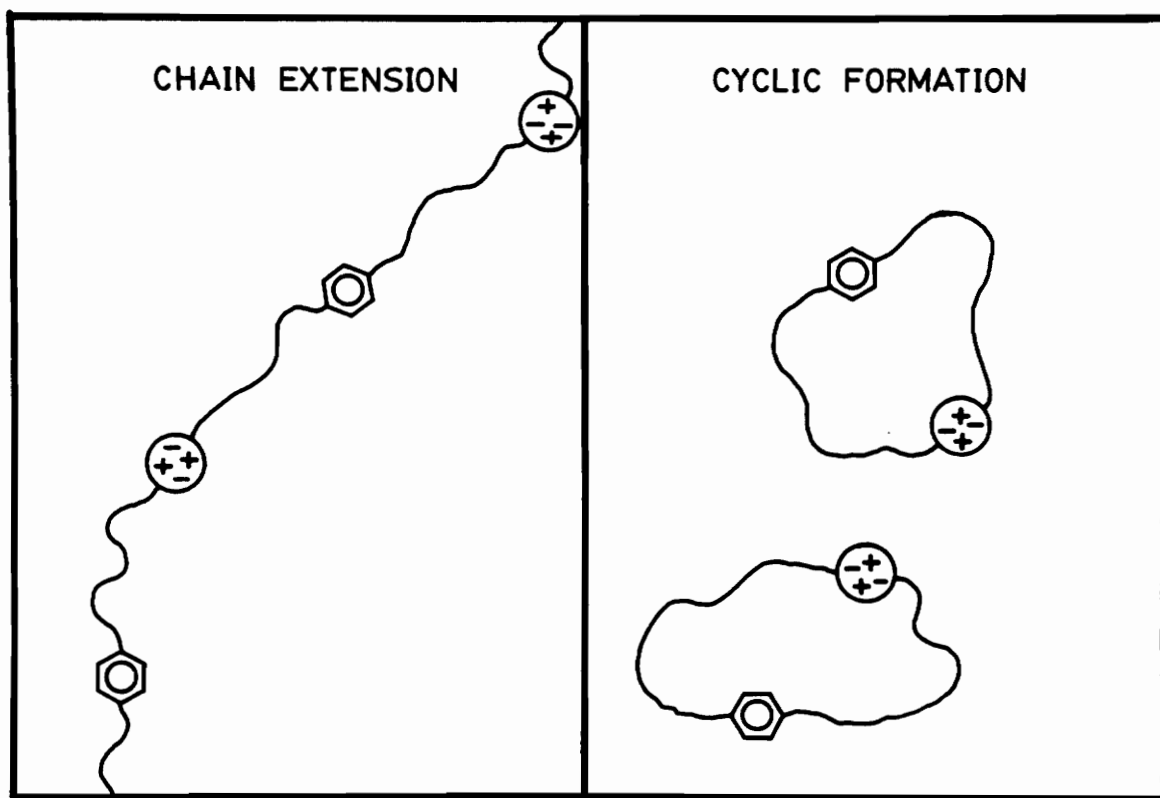


Figure 42. Comparison of chain extension and cyclic structure formation for linear difunctional ionomer.

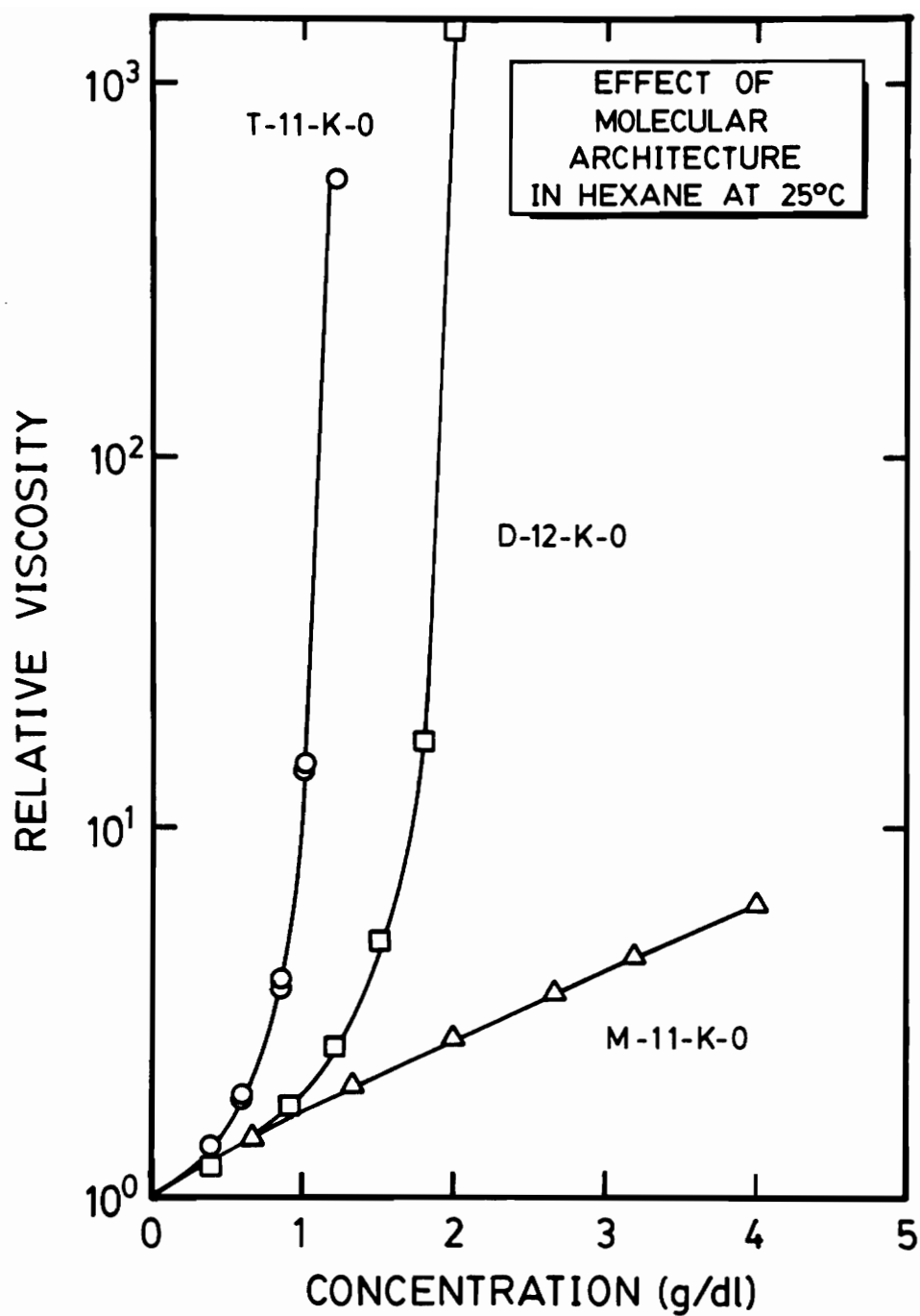


Figure 43. Effect of molecular architecture upon viscosity at an approximately constant molecular weight of 11000-12000.

content is 1.5 times higher. Second, since each three-arm star ionomer already possesses a permanent network junction point, only ion pair association of the terminal ionic groups is necessary for network formation. However, the linear difunctional ionomers do not possess a permanent network junction point, and thus triplets or higher order associations are necessary for network formation. As discussed above, the probability of triplets and higher order associations increases with increasing concentration. Therefore, at the gel concentration for T-11-K-0 the ionic associations are predominantly ion pairs - sufficient for gelation of the three-arm star trifunctional ionomer but not for the linear difunctional ionomer. As concentration increases, the probability of triplet ionic associations (rather than ion pairs) increases until the number of triplets is sufficient for gelation of the difunctional ionomer to occur. These ideas are depicted schematically in Figure 44, where network structures of approximately the same cross-link density are compared. Figure 44a shows that only ion pair association is necessary for network formation of the three-arm star trifunctional ionomer, while Figure 44b shows that triplets (or higher order associations) are required for the linear difunctional ionomer to form a network.

It is of interest to observe the gelation curves of D-12-K-0 and T-11-K-0 on the basis of ionic concentration rather than concentration of polymer. This can be done by using the molecular weight to calculate the moles of molecules per volume from the weight per volume and then multiplying by either 2 or 3, depending upon functionality, to obtain the moles of ions per volume or the ionic concentration. This data is presented in Figure 45. Clearly, for these two ionomers of similar molecular weight but different chain microstructures, the data fall on essentially the same curve. It thus appears, at least in this molecular weight range, that ionic concentration is more important than molecular architecture in determining the gelation concentration. It would certainly be of interest to perform similar studies at other molecular weights to determine if such

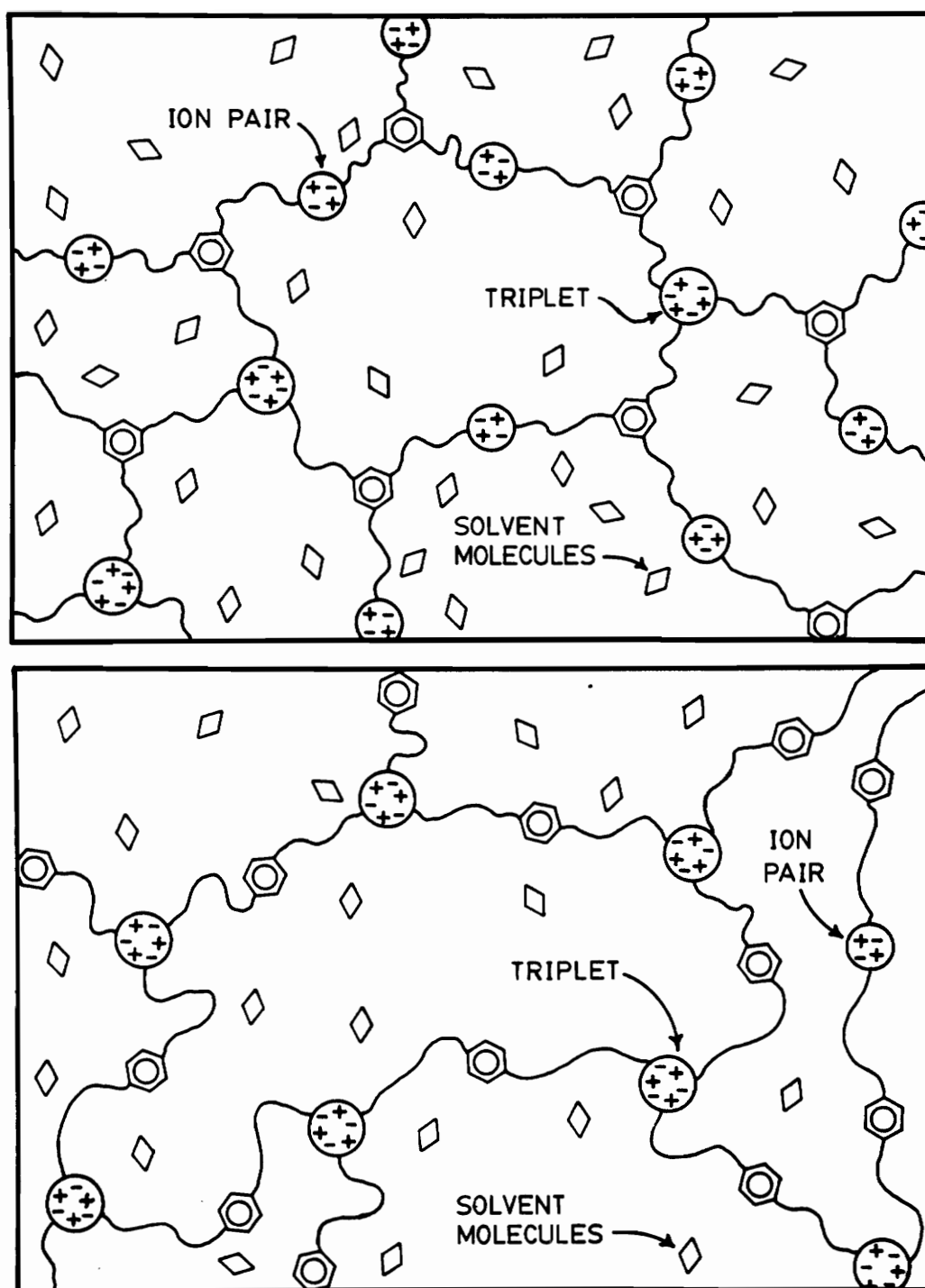


Figure 44. Schematic of ion association resulting in formation of gel structure with similar crosslink density: (a) three-arm star trifunctional ionomer and (b) linear difunctional ionomer.

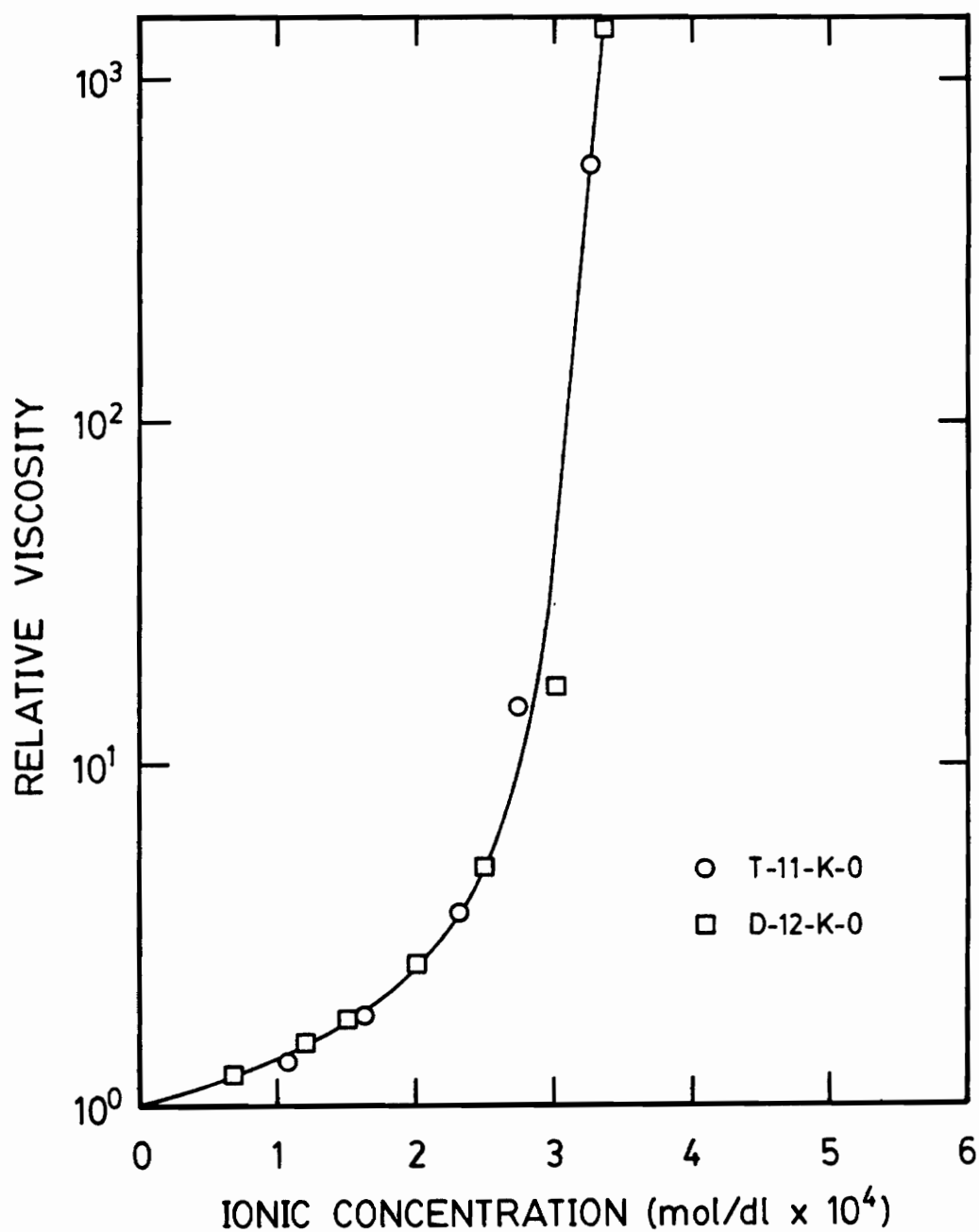


Figure 45. Gelation curves for D-12-K-0 and T-11-K-0 in hexane based on ionic concentration.

behavior is observed over a wide range of molecular weights. However, there is presently no other set of difunctional and trifunctional ionomers with similar molecular weight.

The effect of molecular weight upon the gelation concentration, C_{gel} , of linear telechelic polymers was observed experimentally and predicted theoretically by Broze et al. [106,107] to be given by

$$C_{gel} = k\overline{M}_n^{-1/2} \quad (5.6)$$

where k is a constant depending on the nature of the polymer backbone. The equation was derived by assuming neutralization with alkaline earth metals. It is assumed that the prepolymer chains have a unique and constant end-to-end distance, r , and that the multiplets occupy certain positions within a spatial lattice. Multiplets are assumed to consist of two cations with four chains emerging, thus resulting in a tetrahedral coordination. Lattices with coordination numbers of 6, 8, and 12 are suitable for describing the spatial distribution of multiplets containing three (cubic), four (body-centered cubic), and six (face-centered cubic) cations, respectively. The volume, V , containing one multiplet can be related to the nearest-neighbor distance, r , between multiplets. The relationship $V = ar^3$ results from elementary considerations, where $a = 0.707, 0.769, 1$, and 1.561 for lattices with coordination numbers 12, 8, 6, and 4, respectively. If c is the prepolymer concentration in g/dl, M is the molecular weight (for monodisperse polymers), and N_0 is Avogadro's number, then the mean number of divalent cations per unit volume is cN_0/M and the mean number of cations per multiplet, \bar{n} , is given by

$$\bar{n} = ar^3 \frac{cN_0}{M} = \frac{ar^3}{166} \frac{c}{M} \quad (5.7)$$

Of course, r is not really a constant for polymers and the root-mean-square end-to-end distance, $\langle r^2 \rangle^{1/2}$, is normally used as an average. Therefore, it is necessary in equation (5.7) to use the mean cubic value of r , or $\langle r^3 \rangle$. The relationship between $\langle r^2 \rangle$ and $\langle r^3 \rangle$ is given by

$$\langle r^3 \rangle^{1/3} = 1.07 \langle r^2 \rangle^{1/2} \quad (5.8)$$

Substituting $\langle r^3 \rangle$ for r^3 in equation (5.7) gives

$$\bar{n} = \frac{1.23a}{166} \langle r^2 \rangle^{3/2} \frac{c}{M} \quad (5.9)$$

The root-mean-square end-to-end distance may also be given by

$$\langle r^2 \rangle^{1/2} = \alpha \langle r_0^2 \rangle^{1/2} \quad (5.10)$$

where $\langle r_0^2 \rangle^{1/2}$ is the unperturbed root-mean-square end-to-end distance and α is the intramolecular expansion coefficient. Making this substitution and replacing M with \bar{M}_n gives

$$\bar{n} = 7.4 \times 10^{-3} a_{\bar{n}} \left[\frac{\langle r_0^2 \rangle}{M} \right]^{3/2} \alpha^3 c \bar{M}_n^{1/2} \quad (5.11)$$

The parameter $a_{\bar{n}}$ is well defined for all integer values of \bar{n} . For non-integer values it is given by

$$a_{2 \leq \bar{n} \leq 3} = 2.683 - 0.561\bar{n} \quad (5.12a)$$

$$a_{3 \leq \bar{n} \leq 4} = 1.693 - 0.231\bar{n} \quad (5.12b)$$

$$a_{4 \leq \bar{n} \leq 6} = 0.385(6 - \bar{n}) + 0.354(\bar{n} - 4) \quad (5.12c)$$

Thus the multiplet size depends upon the prepolymer concentration and the molecular weight, intrinsic flexibility ($\langle r_0^2 \rangle / M$), and the expansion coefficient for a given solvent and temperature.

Broze et al. [107] further suggest that for linear telechelic polymers neutralized with alkaline earth cations (resulting in a functionality of two for both metal and prepolymer), the critical gelation concentration corresponds to only one cation per multiplet ($\bar{n}_{gel} = 1$). This, however, assumes the formation of stable bonds. The ionic associations formed in ionomers are not permanent, but are thermolabile and have a characteristic lifetime which depends upon temperature, the dielectric constant of the medium, and the nature of the ion pairs. Thus \bar{n}_{gel} must be greater than 1 for gelation to occur.

For a given set of conditions, \bar{n}_{gel} is a constant. Thus equation (5.11) can be rearranged to give

$$\frac{\bar{n}_{gel}}{7.4 \times 10^{-3} a_{\bar{n}_{gel}}} = \left[\frac{\langle r^2 \rangle}{M} \right] C_{gel} \bar{M}^{1/2} = K \quad (5.13)$$

where K is a constant for a given alkaline earth cation, solvent, and temperature. The value of $\langle r^2 \rangle / M$ can be assumed to be independent of M up to an M of about 50,000. Therefore, equation (5.13) leads to the previously given equation (5.6), i.e.

$$C_{gel} = k \bar{M}_n^{-1/2}. \quad (5.6)$$

This equation was found by Broze et al. [106] to fit experimental data for several types of linear telechelic polymers for which the dispersity index ranged from less than 1.2 to 1.8. The effect of molecular weight upon viscosity behavior of the three-arm star trifunctional ionomer, $\bar{M}_n = 11000, 14000, \text{ and } 34000$, is shown in Figure 46. (T-8.3-K-0 swells but is not soluble at these low concentrations due to the high concentration of

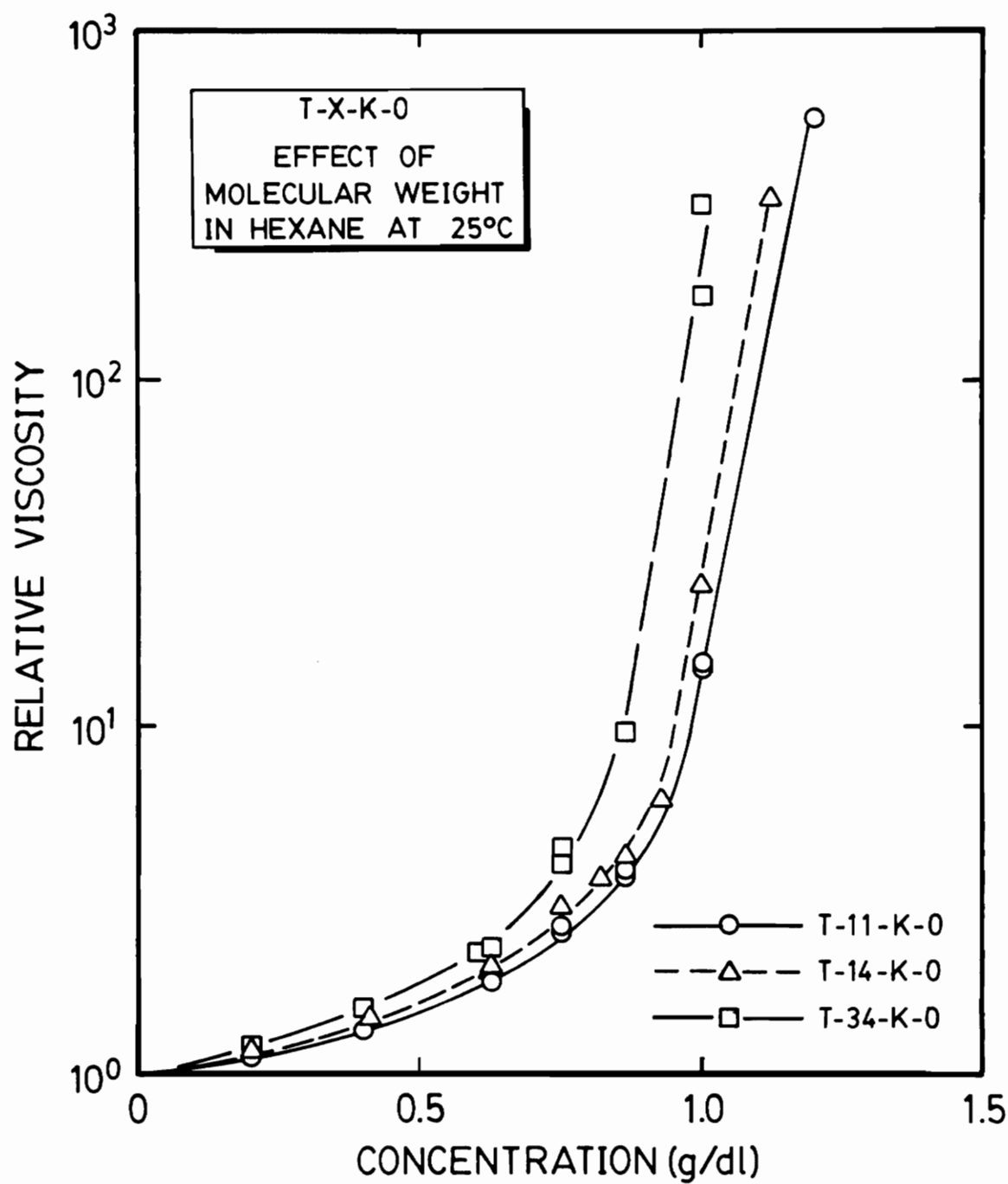


Figure 46. Effect of molecular weight upon the viscosity-concentration behavior of the three-arm star trifunctional ionomer.

ionic groups.) The gelation curves for the three trifunctional ionomers occur in the order predicted by equation (5.6) for linear difunctional ionomers, i.e. gelation concentration decreases with increasing molecular weight. However, the exponent for the trifunctional molecules is -0.11 rather than -0.5, so that molecular weight has less of an effect for these ionomers compared to those studied by Broze et al. This may be due to the difference in both the nature of the ionic groups and the molecular architecture. The value of k is 3.16. The plot of $\log C_{gel}$ vs. $\log \overline{M}_n$ from which the values of k and the exponent were determined is shown in Figure 47.

Figure 48 shows the effect of molecular weight upon the gelation behavior of the linear difunctional ionomer neutralized with KOH. The trend here is different from that observed by Broze et al. [107] for the carboxylated elastomeric telechelic ionomers and different also from that reported here for the three-arm star sulfonated polyisobutylene telechelic ionomers. That is, the low molecular weight ionomer, D-6.5-K-0, gels at a lower concentration than the higher molecular weight ionomer, D-12-K-0. Even though the trend observed for these ionomers is different, it does agree with the idea that higher ion concentrations result in a higher degree of association leading to gelation at lower concentrations. It is possible that in this low molecular weight region the ionic concentration may be more important than the molecular weight. As molecular weight increases there may be a point where molecular weight becomes the important variable due to the occurrence of entanglements, resulting in a decrease of the gelation concentration as molecular weight increases. Such a transition has been observed for the bulk G' in carboxylated elastomeric telechelic ionomers by Jérôme and Broze (see Figure 9 on page 35) and is reported in this dissertation for the sulfonated polyisobutylene telechelic ionomers (see Figure 36 on page 101). This transition has not, however, been observed in solutions. In order to test this hypothesis, it would be necessary to investigate the gelation behavior of a broader series of molecular weights, beginning at about

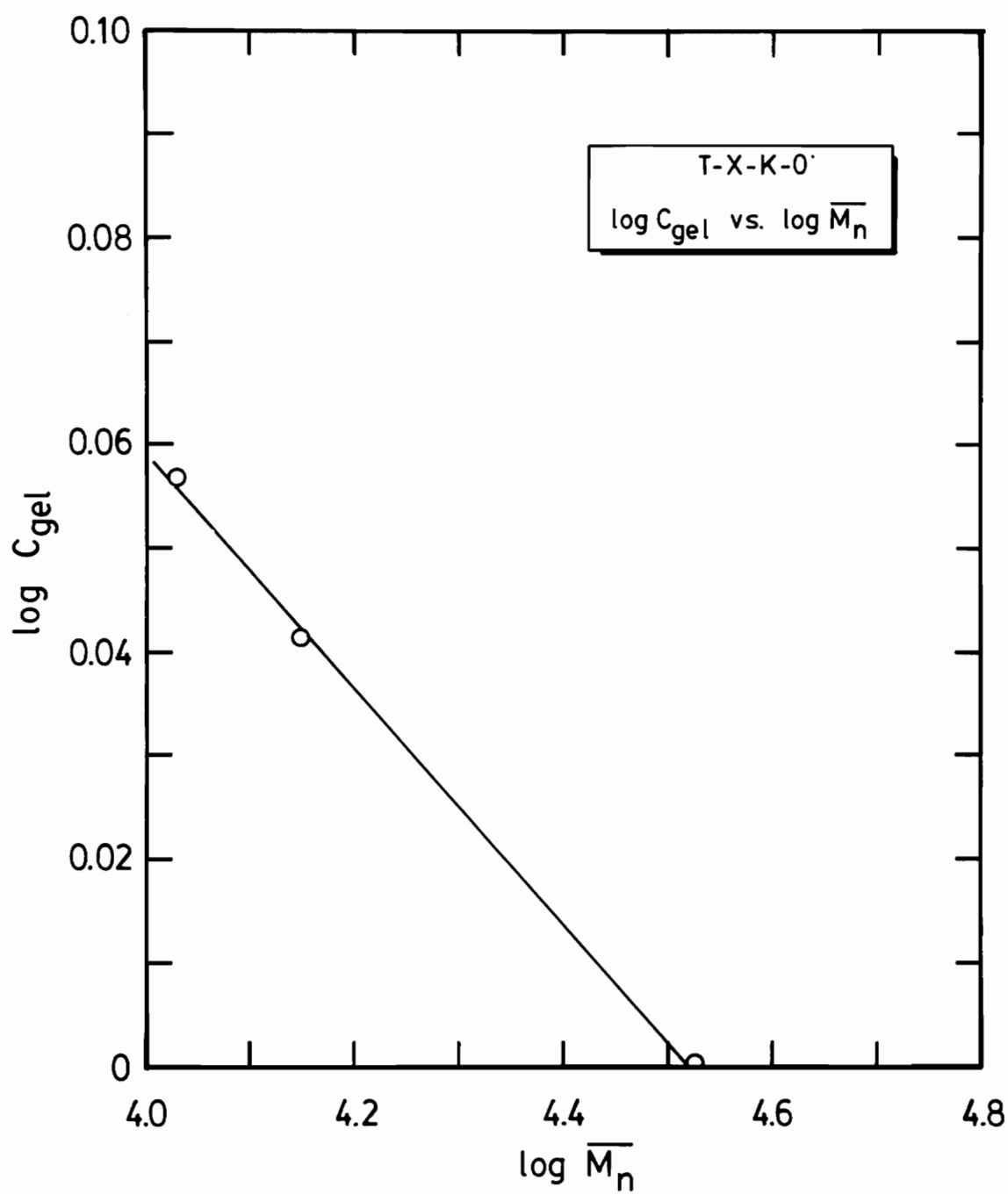


Figure 47. Plot of log of gelation concentration vs. log of molecular weight for three-arm star trifunctional ionomers.

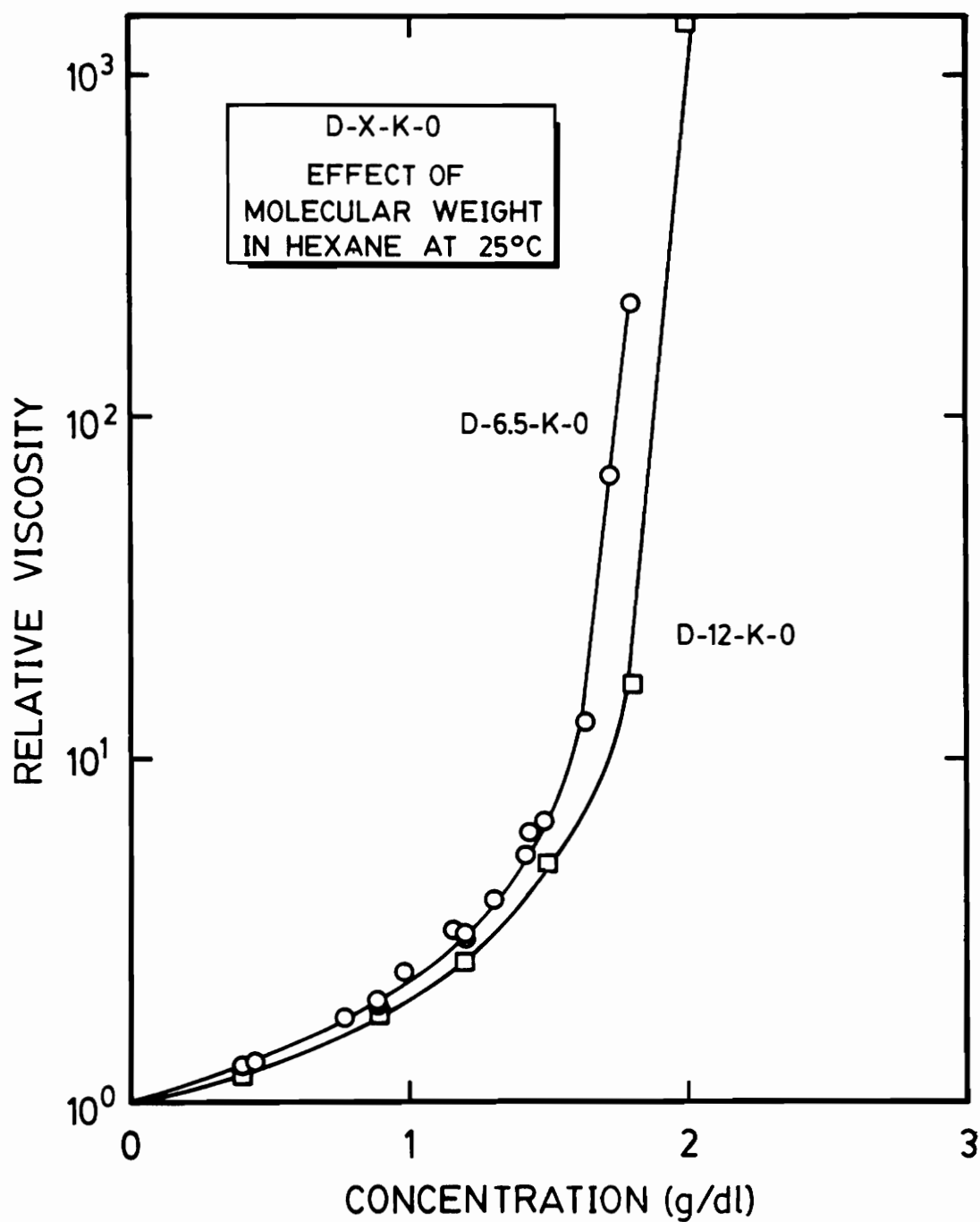


Figure 48. Effect of molecular weight upon the viscosity-concentration behavior for the linear difunctional ionomers.

4000 or so and extending up to at least 25000. Unfortunately, the only linear difunctional ionomers available were the 6500 and 12000 \overline{M}_n materials.

The fact that excess neutralizing agent strongly affects the solid state mechanical and melt rheological properties of the sulfonated polyisobutylene telechelic ionomers suggests that this variable may also have a strong effect upon the viscosity behavior in nonpolar solvents. Figures 49 and 50 show the effect of both the type of neutralizing agent and excess neutralizing agent upon the viscosity behavior in hexane of the D-6.5 and D-12 materials, respectively. For the D-6.5 series the gelation curves for D-6.5-K-0, D-6.5-Ca-0, and D-6.5-Ca-100 are essentially the same, while D-6.5-K-100 apparently gels at a slightly lower concentration. It is not clear why the D-6.5-K-100 should associate more strongly in solution than the D-6.5-Ca-100. The difference cannot be attributed to experimental error in the measurements, since the viscosities were found to be quite reproducible. It also cannot be attributed to the difference in number of cations present (twice as many K^+ as Ca^{2+}) since the D-12 materials show somewhat different behavior. In Figure 50 it is clear that at each concentration (except the highest) the viscosities of the D-12 solutions containing excess neutralizing agent, for *both* potassium and calcium, is higher than that of the solutions of stoichiometrically neutralized material. Thus, excess neutralizing agent results in somewhat stronger association but not to the extent found for bulk properties. Excess neutralizing agent can have an extremely large effect on bulk properties. The likely reason for the smaller effect in solution is that much of the excess neutralizing agent is dispersed in the solvent leaving less of the excess neutralizing agent associated with the ionic regions. Thus less reinforcement of the ionic associations occurs due to the dilution of the excess neutralizing agent. Figure 50 also shows the behavior of the D-12-ZnAc-100 solution. The weaker association of zinc due to its less ionic, more coordinative bonding has already been discussed. Clearly, this association is also weaker in solution since gelation occurs at a higher concentration.

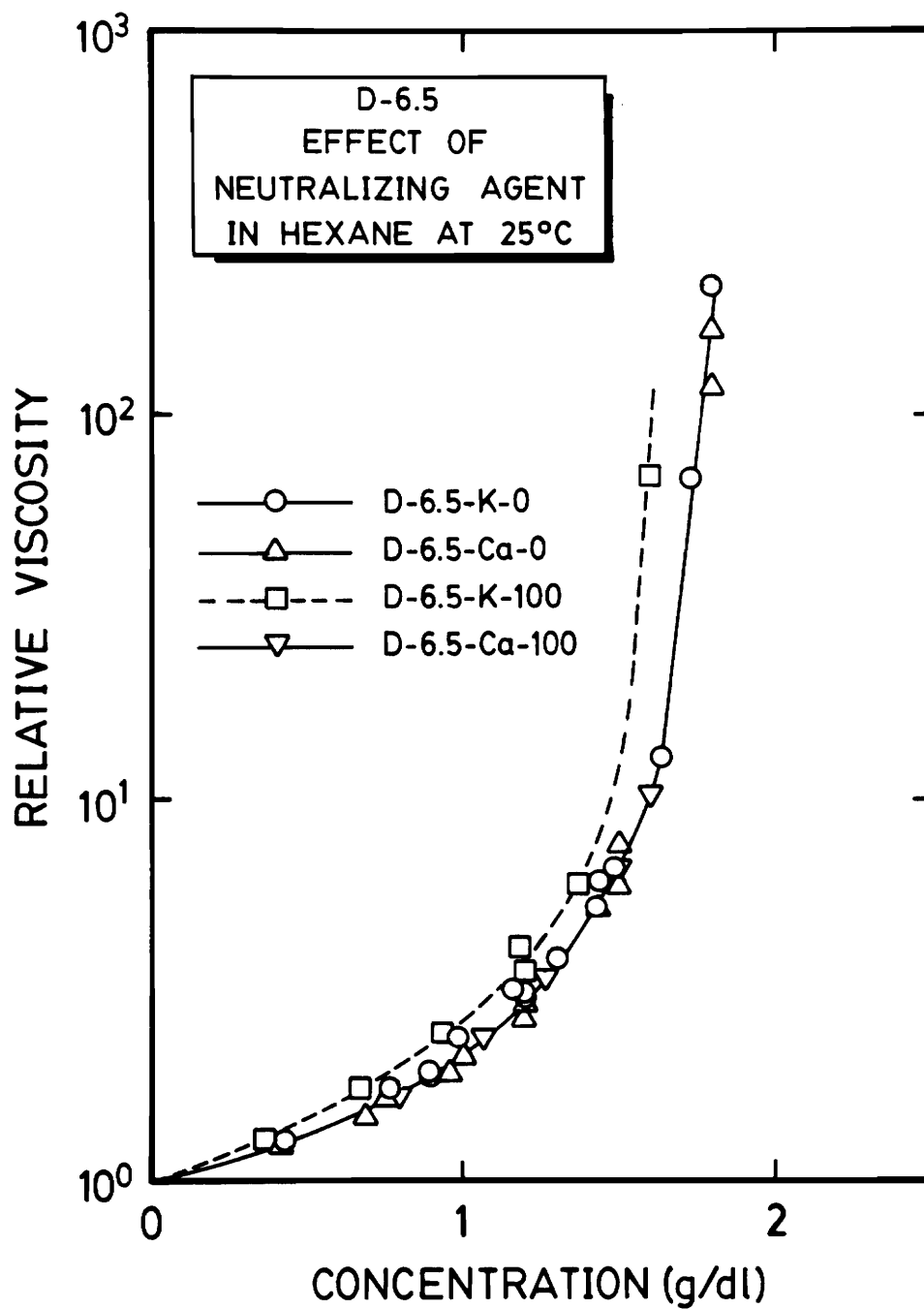


Figure 49. Effect of neutralizing agent and excess neutralizing agent on viscosity behavior of D-6.5 in hexane.

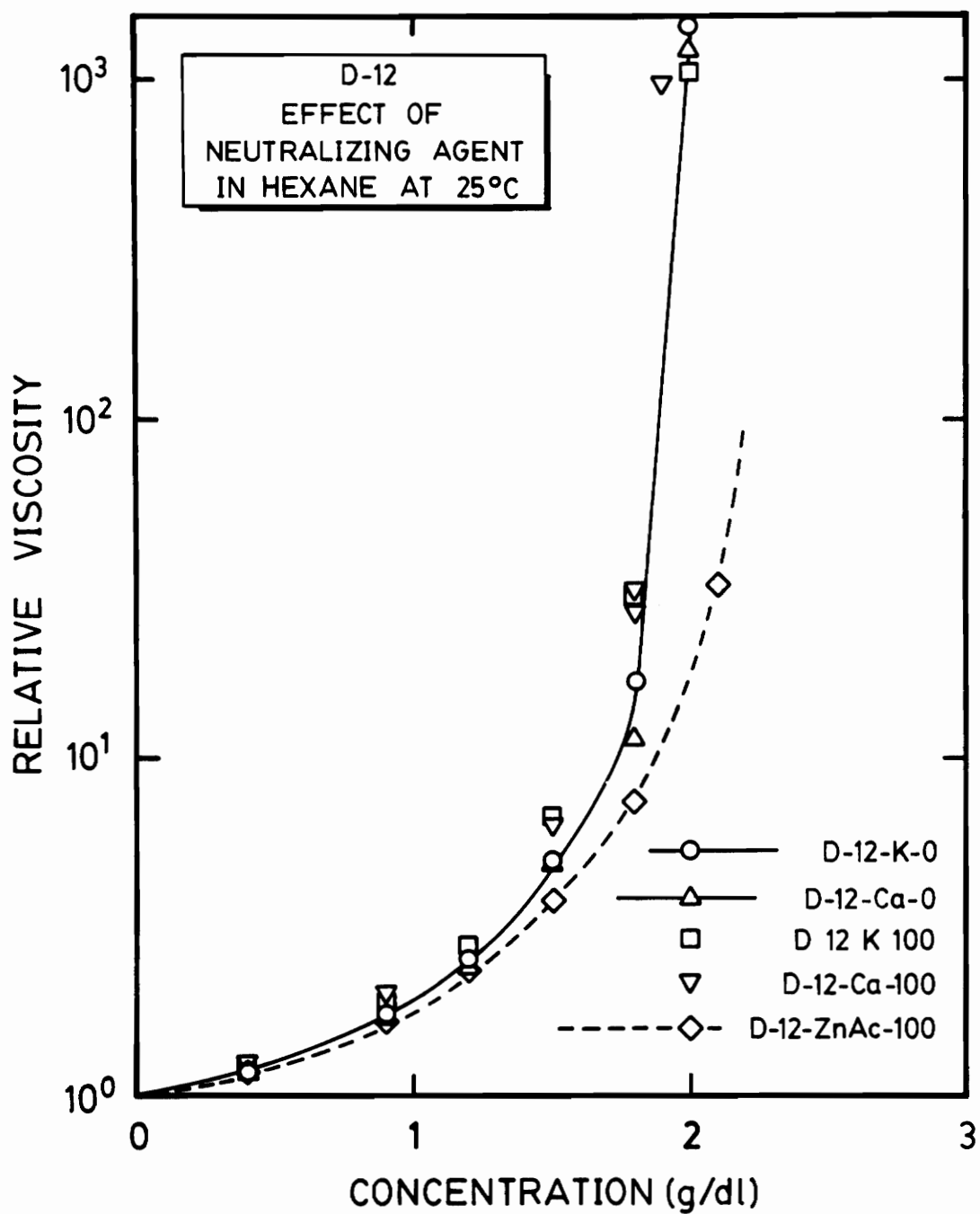


Figure 50. Effect of neutralizing agent and excess neutralizing agent on viscosity behavior of D-12 in hexane.

Figure 51 shows the viscosity behavior of T-11-K-0 in two different solvents - hexane and tetrahydrofuran (THF). The gelation in hexane due to the strong interaction of the ionic groups in a nonpolar medium has already been discussed. In THF, a more polar solvent, the solvent molecules interact more strongly with the ionic groups on the polymer chains. Thus the ionic groups interact less strongly with each other and the viscosity is greatly reduced. Clearly, the type of solvent has a large effect upon the strength of association of the ionic groups.

Nonpolar-Polar Solvent Mixtures

In typical fluids, both low molecular weight substances and high polymers, viscosity is normally observed to decrease with increasing temperature. This decrease in viscosity is due to the higher thermal energy which causes more rapid molecular motions and more free volume in which these motions may occur. Figure 52 illustrates the typical temperature dependent viscosity of a fluid, this particular fluid happening to be solutions of D-12-K-0 in decahydronaphthalene (decalin or DHN) at several different concentrations. The viscosity is observed to decrease with temperature as would be expected. However, something unusual occurs when a small amount of a more polar solvent, such as hexanol, is added to an ionomer solution in a nonpolar solvent such as decalin. As discussed in Chapter II, Lundberg and Makowski [115] observed that such solutions may display unusual behavior in that the viscosity may increase, remain relatively constant, or display maxima or minima over broad temperature ranges. They interpret this behavior using the equilibrium

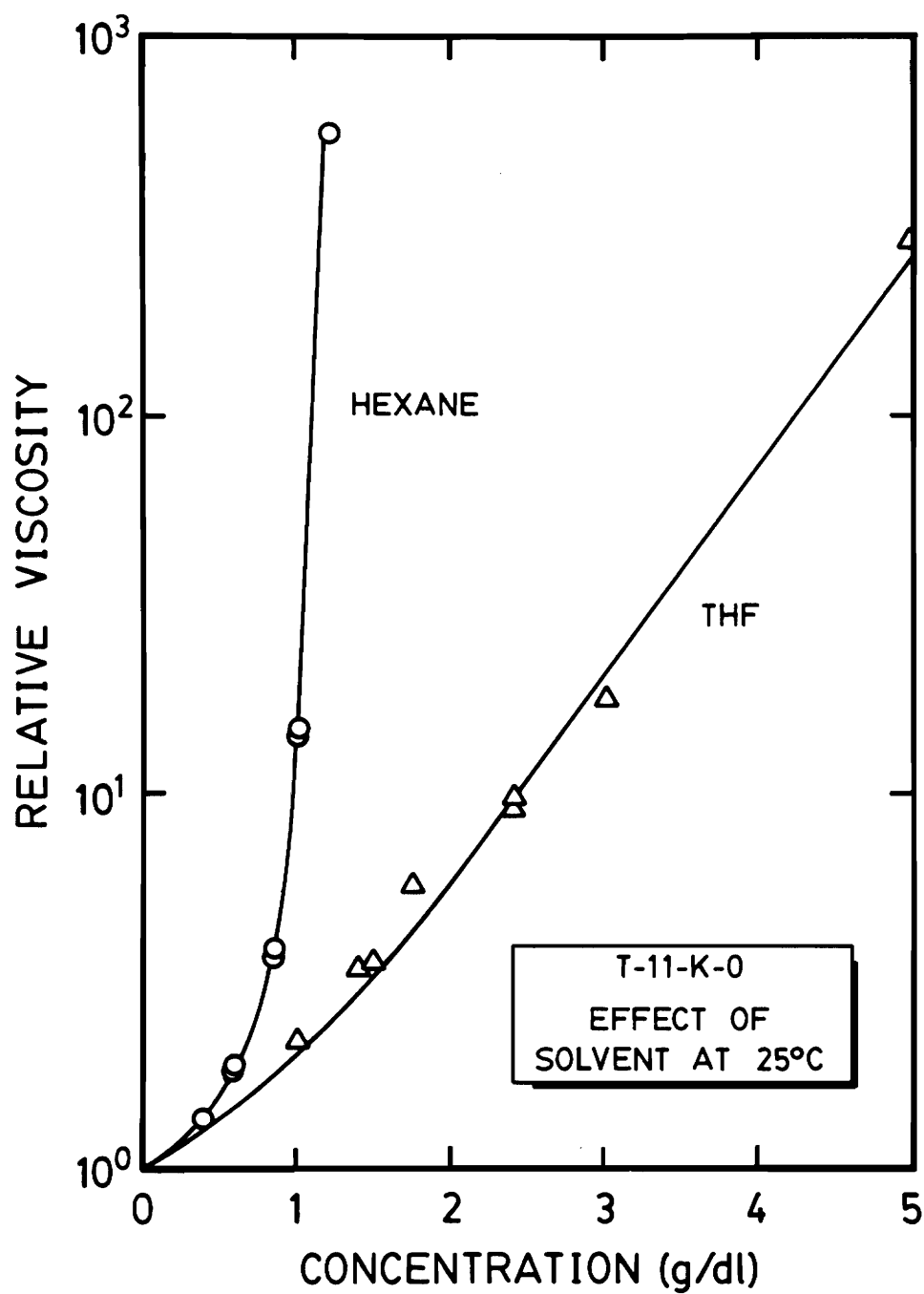


Figure 51. Viscosity behavior of T-11-K-0 in hexane and THF.

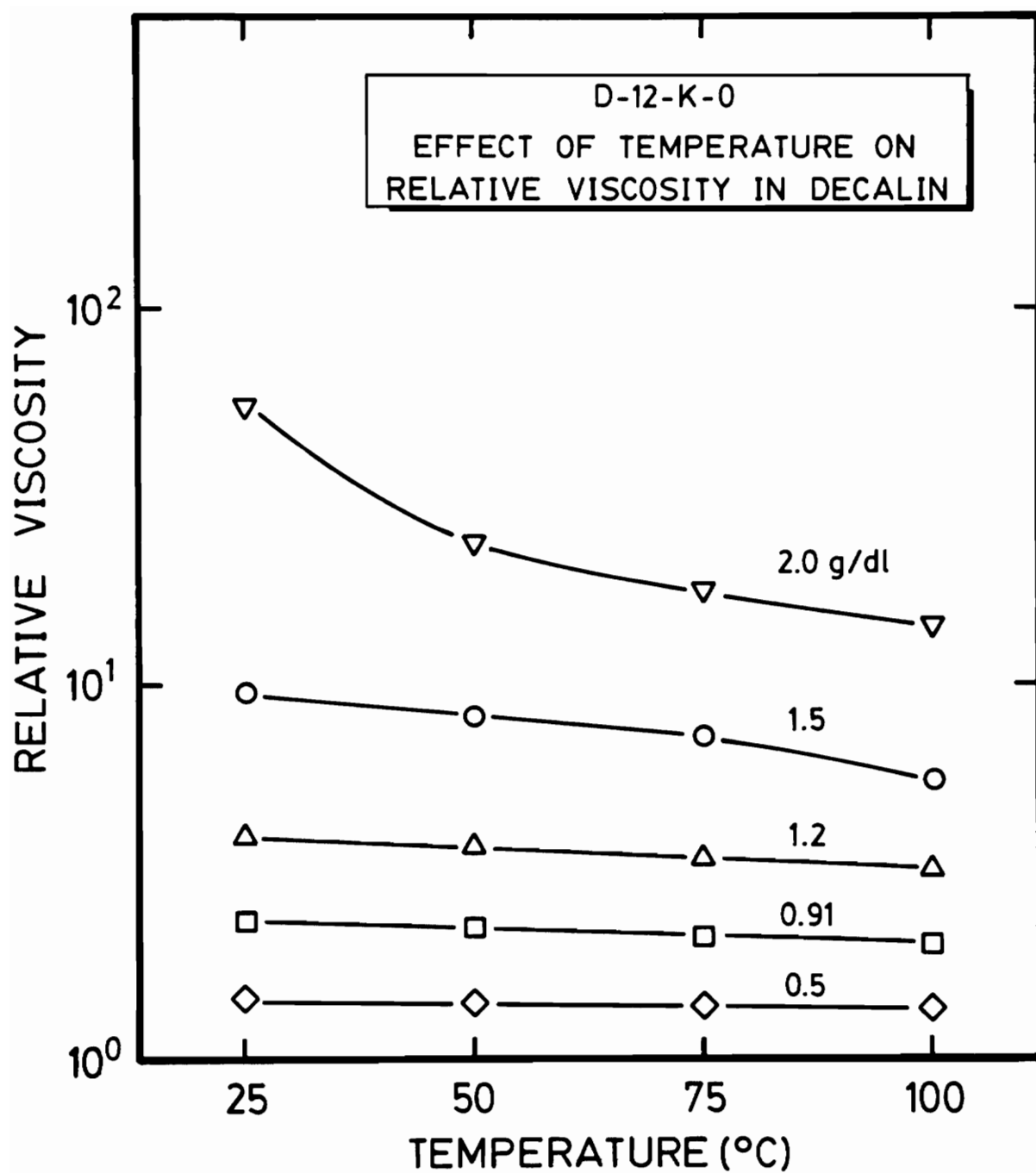
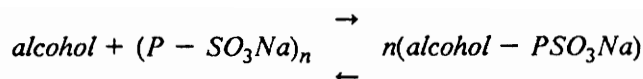


Figure 52. Effect of temperature on relative viscosity of D-12-K-0 in decalin.



where the associating species ($P - SO_3Na$) is favored at high temperatures, while the solvated species ($\text{alcohol} - PSO_3Na$) is favored at lower temperatures. These workers do admit that this is an oversimplification since it ignores the hydrocarbon solvent and the polymer backbone. At higher temperatures the strength of the ionic interactions is decreased and thus the viscosity begins to decrease again. Infrared spectroscopy as well as electron spin resonance are currently being used to study these types of ionic interactions by Weiss [138].

Figure 53 shows the effect of temperature on the kinematic viscosity of T-11-K-0 in a 2% hexanol-98% decalin mixture at three different concentrations. At a concentration of 0.9 g/dl the kinematic viscosity decreases over the entire temperature range studied, i.e. 25-80°C. At 1.2 g/dl the kinematic viscosity is relatively constant over this temperature range. Upon increasing the concentration from 1.2 to 1.5 g/dl, the kinematic viscosity is observed to decrease slightly from 25 to 45°C. It then increases dramatically in the temperature range from 45°C to 80°C, increasing by a factor of 2.5. Figure 54 shows this same data plotted in terms of relative viscosity instead of kinematic viscosity. Since the relative viscosity is simply the kinematic viscosity of the solution divided by the kinematic viscosity of the solvent, the effect of the decreasing solvent viscosity is removed in these data. Thus what is being observed is the effect of temperature upon the solute itself. For this particular case the relative viscosity increases throughout the temperature range of 45-80°C at all three concentrations and the effect becomes stronger with increasing concentration and increasing temperature. The fact that the effect increases with increasing concentration must certainly be because of the more extensive interaction of the ionic groups at higher concentrations.

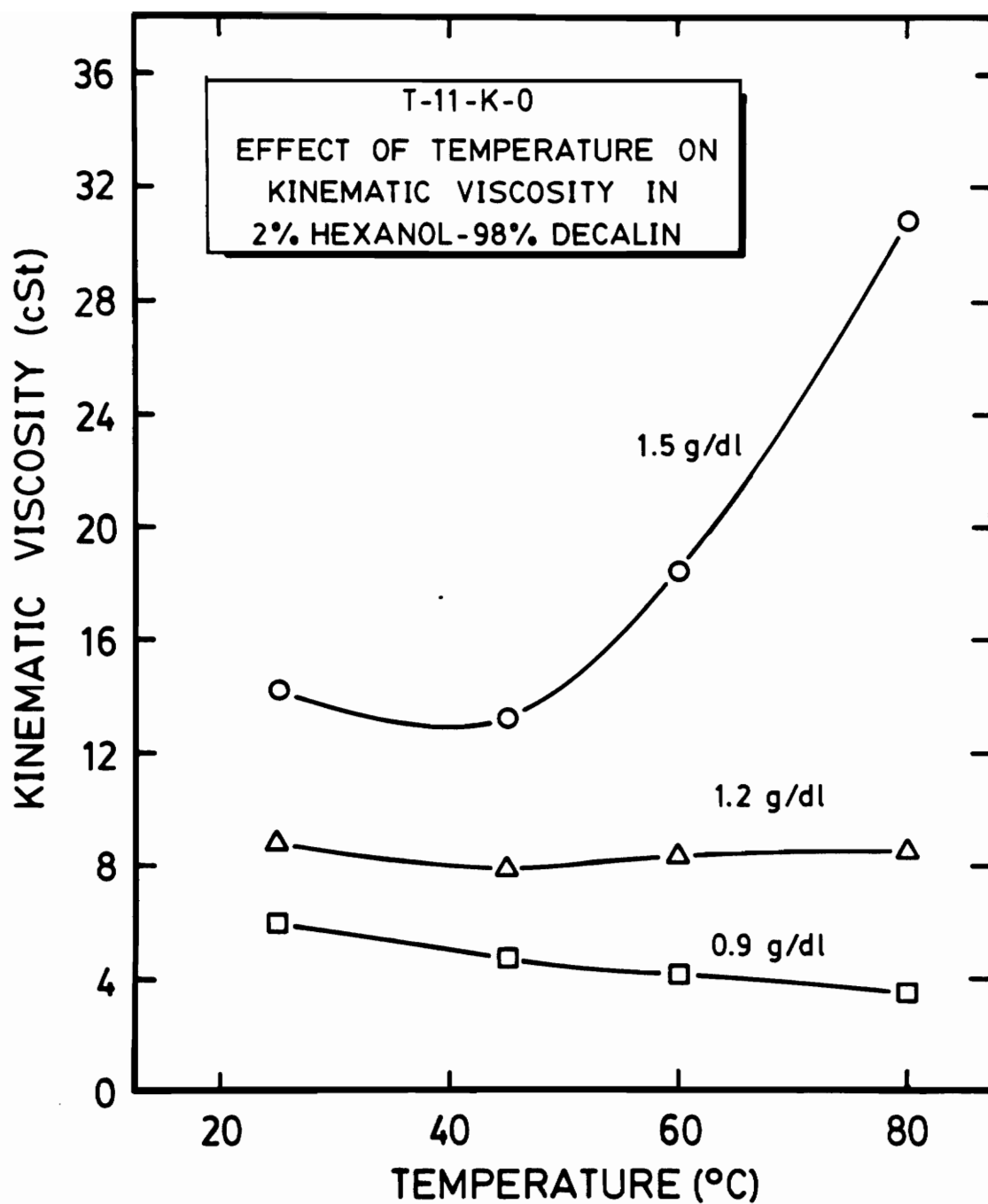


Figure 53. Effect of temperature on kinematic viscosity of T-11-K-0 in 2% hexanol-98% decalin.

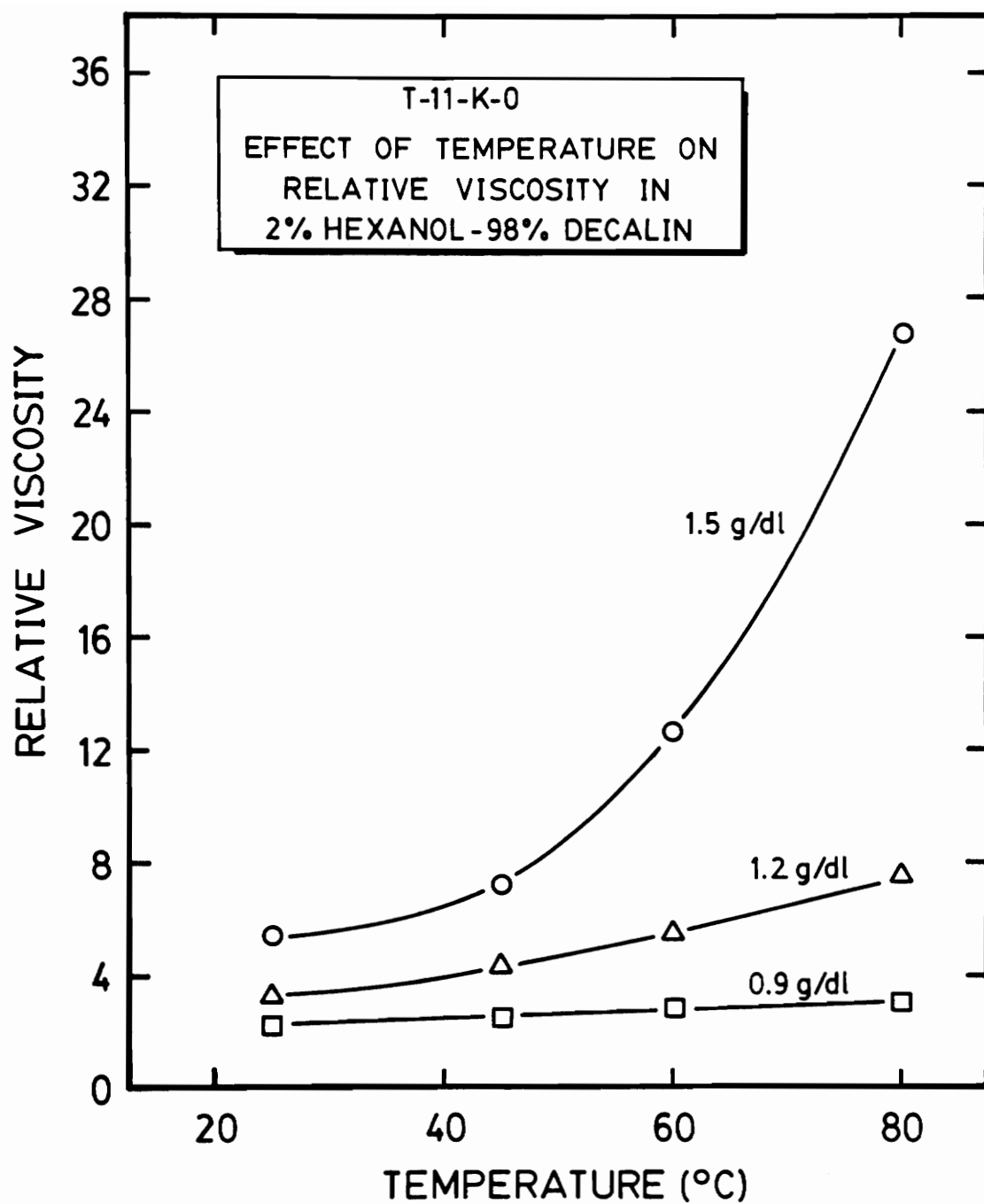


Figure 54. Effect of temperature on relative viscosity of T-11-K-0 in 2% hexanol-98% decalin.

Figures 55 and 56 show the effect of temperature upon the kinematic and relative viscosities, respectively, of D-12-K-0 at a concentration of 1.5 g/dl in hexanol/decalin mixtures containing 0.5, 1.0, and 2.0% hexanol. Clearly the kinematic viscosity of all three solutions steadily decreases as temperature is increased from 25 to 80°C. The relative viscosity, however, is observed to increase except for the lowest hexanol content between 60°C and 80°C. This behavior might be interpreted in the following way. At room temperature the hexanol is dispersed between the ionic regions, which it tends to solvate, and the remainder of the solution. As temperature increases the polar hexanol molecules become more soluble in the nonpolar decalin, and thus the equilibrium changes. As the polar hexanol molecules are removed from the ionic aggregates, the aggregates associate more strongly and the viscosity increases. The reason for the decrease in relative viscosity for the 0.5% hexanol mixture between 60 and 80°C is not clear. There might be a critical number of hexanol molecules associated with the ionic aggregates which will remain associated no matter how high the solubility of hexanol in decalin becomes. This critical point would be expected to be reached at a lower temperature for the solution with the lowest concentration of hexanol, as is observed.

Figures 57 and 58 show the same type of data for the same material, D-12-K-0, except at a concentration of 2.0 instead of 1.5 g/dl. The behavior is clearly quite similar except that the viscosity increases with temperature are much stronger, since the molecules interact with one another much more at this higher concentration. Figure 59 shows this same data plotted in terms of relative viscosity vs. percent hexanol at each of the four different temperatures. There is a sharp decrease in the relative viscosity at each temperature up to 1% hexanol. Above this hexanol content the further decreases in viscosity become progressively smaller until at a 5% hexanol concentration the viscosities at all four temperatures are the same. Lundberg and Makowski [115] have observed similar behavior for sulfonated polystyrene in mixed solvents, and have sug-

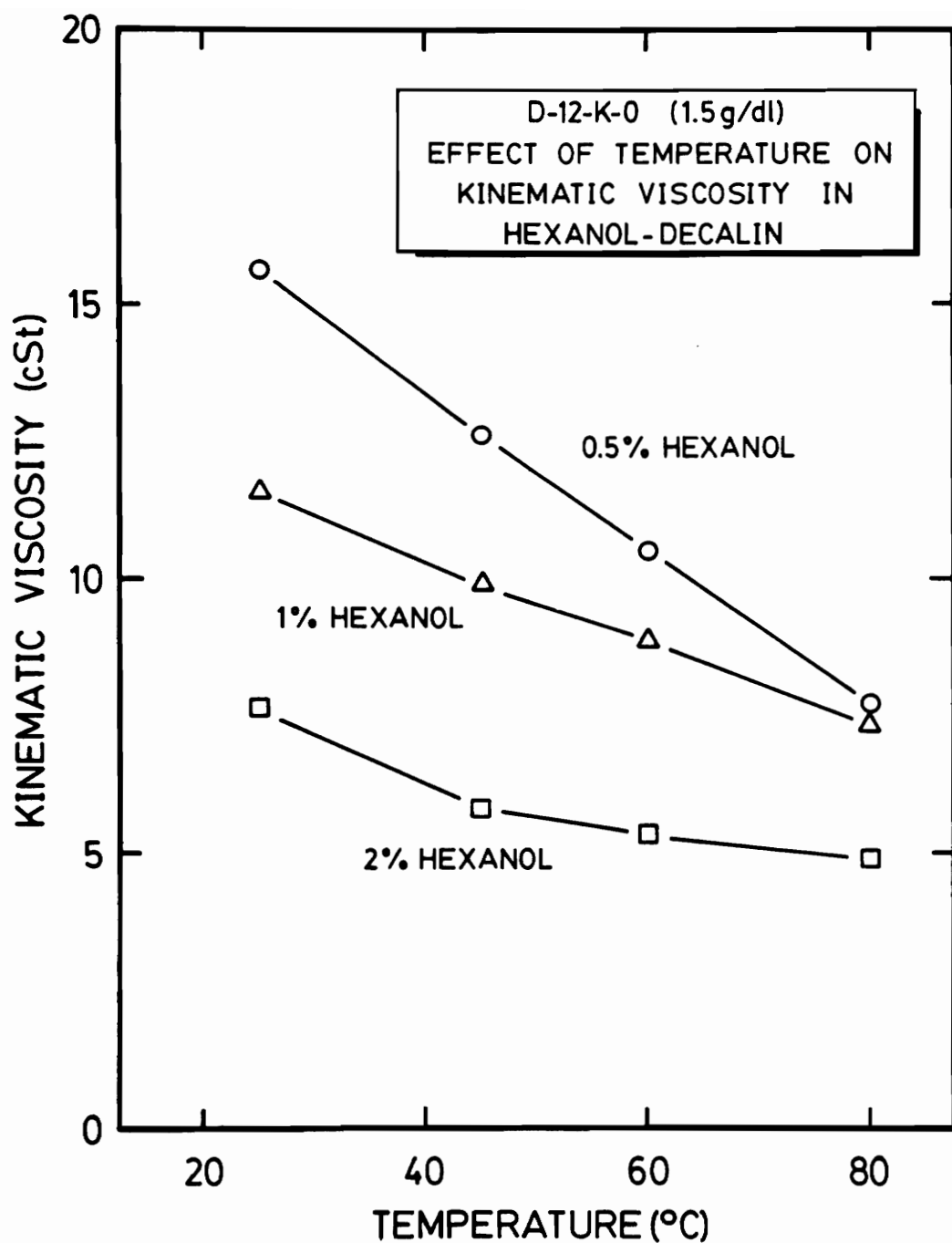


Figure 55. Effect of temperature on kinematic viscosity of D-12-K-0 at a concentration of 1.5 g/dl in hexanol/decalin.

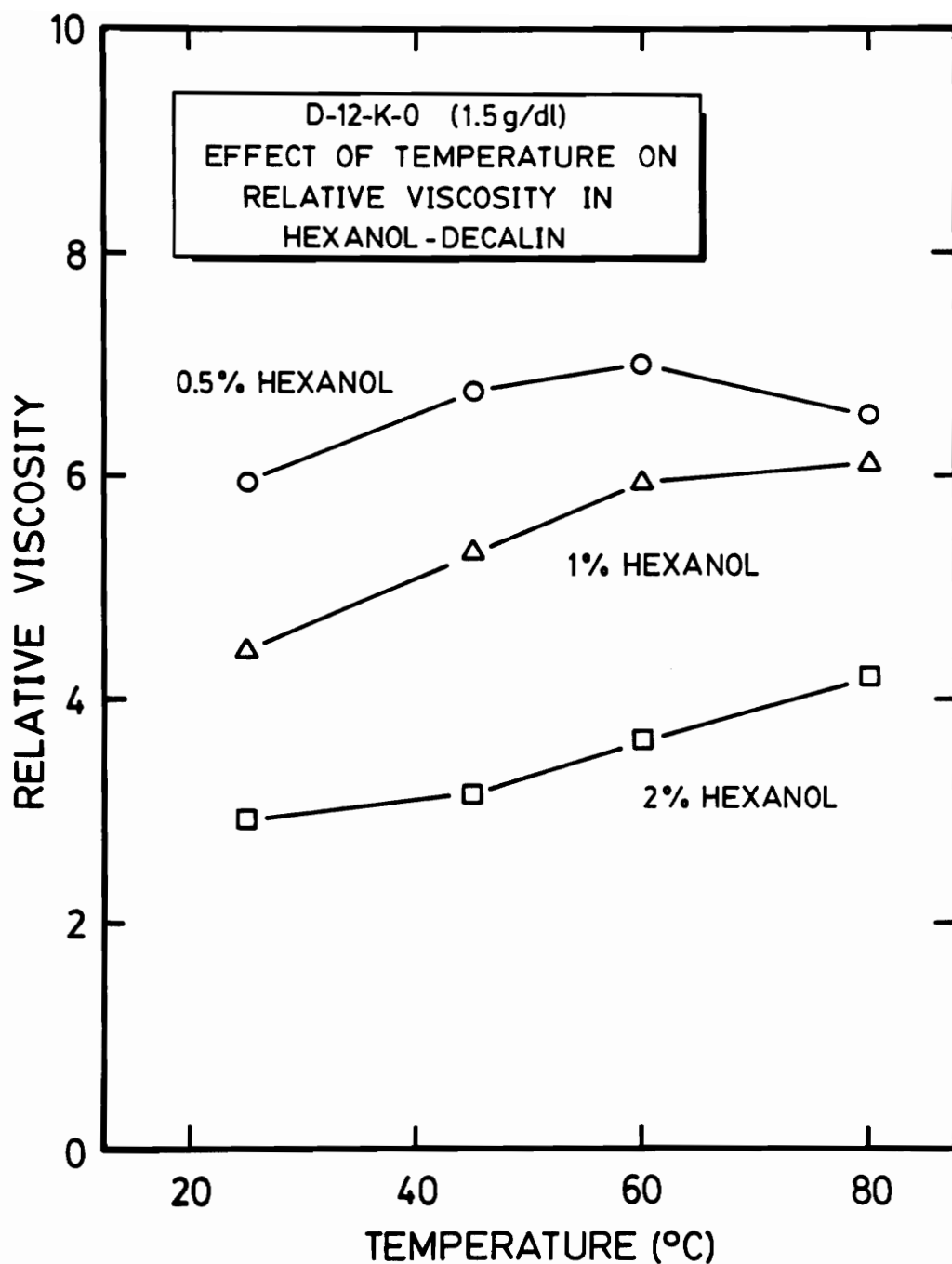


Figure 56. Effect of temperature on relative viscosity of D-12-K-0 at a concentration of 1.5 g/dl in hexanol/decalin.

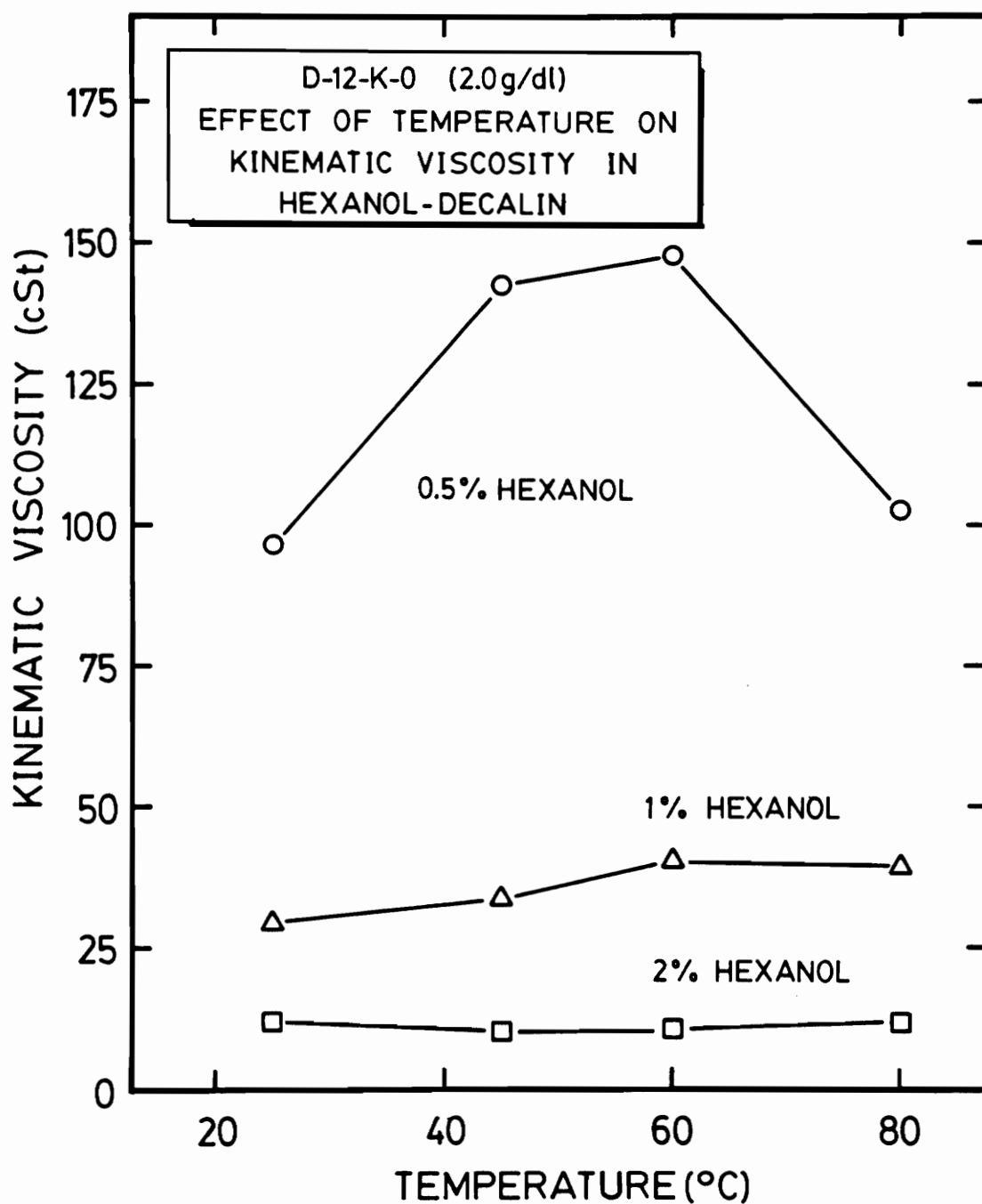


Figure 57. Effect of temperature on kinematic viscosity of D-12-K-0 at a concentration of 2.0 g/dl in hexanol/decalin.

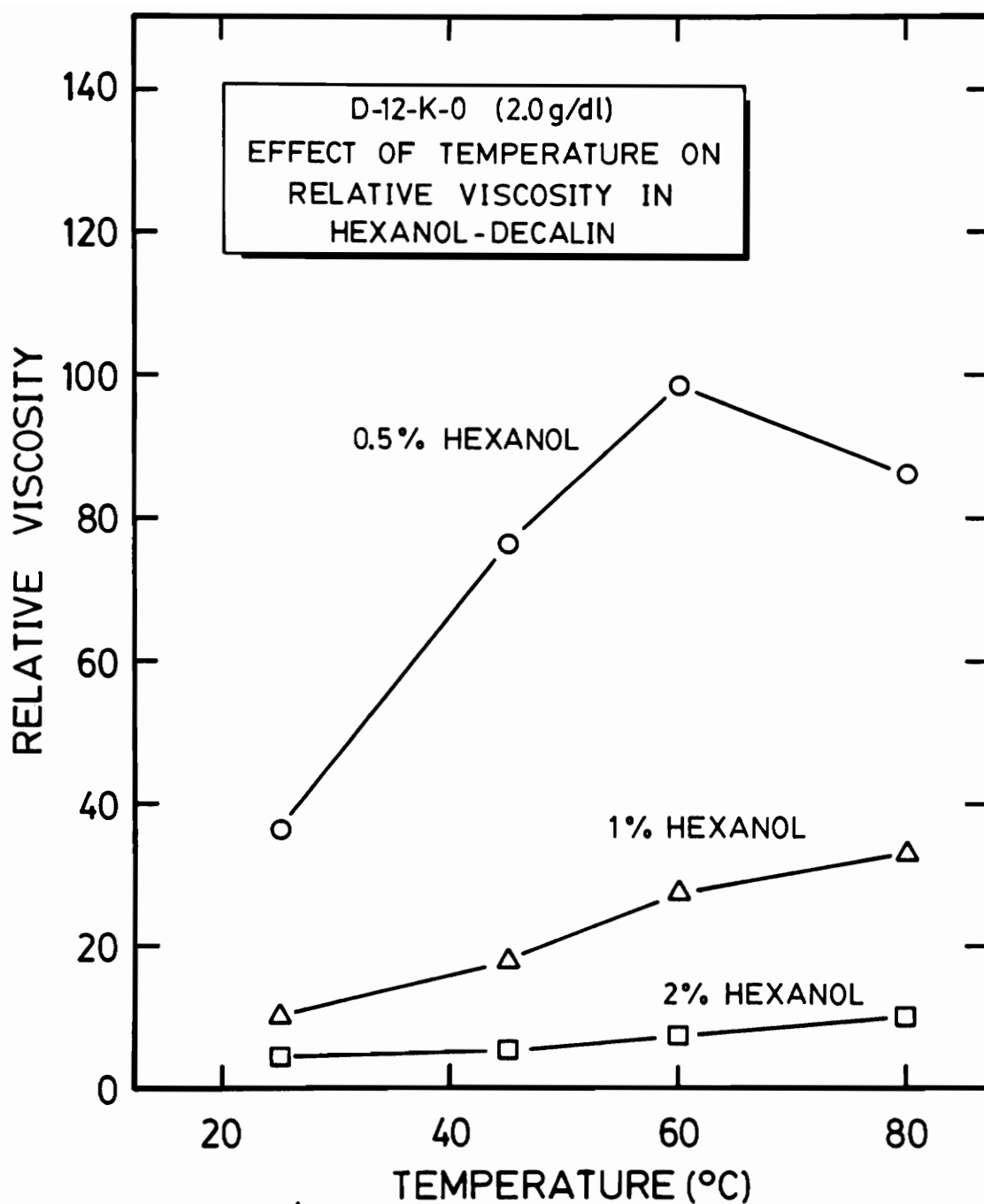


Figure 58. Effect of temperature on relative viscosity of D-12-K-0 at a concentration of 2.0 g/dl in hexanol/decalin.

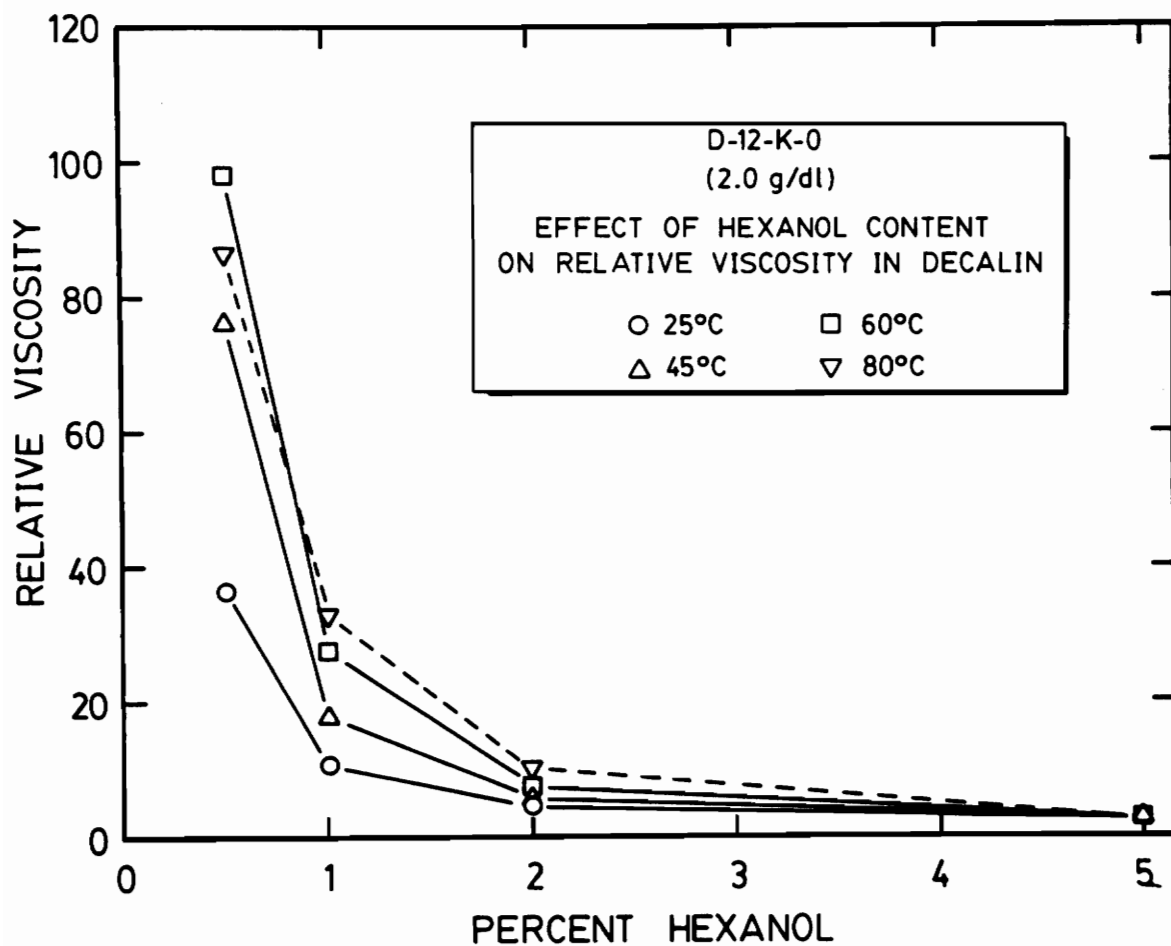


Figure 59. Effect of hexanol content on relative viscosity of D-12-K-0 at a concentration 2.0 g/dl.

gested that as more polar cosolvent is added the ionic groups are, in a way, being "titrated". It is clear that the "endpoint" in this case must be near 1% to 2% hexanol since further addition of hexanol has little effect upon viscosity.

Figures 60 and 61 compare the kinematic and relative viscosities, respectively, for D-6.5-K-0 and D-12-K-0 at a concentration of 2 g/dl in 1% hexanol-99% decalin. Clearly, the increase in viscosity is much greater for the D-6.5 solution than for the D-12 solution because there are almost twice as many ionic groups present. Between 25°C and 80°C the D-12-K-0 solution experiences a kinematic viscosity increase of 37% and a relative viscosity increase of 175%, while the D-6.5-K-0 solution experiences a kinematic viscosity increase of 360% and a relative viscosity increase of 870%! Thus very low concentrations of ionomer may result in phenomenal viscosity increases with increasing temperature.

The kinetics of these viscosity changes are also of importance. Figure 62 shows the time dependent relative viscosity of D-6.5-K-0 at a concentration of 2.0 g/dl in 1% hexanol-99% decalin following a temperature jump from 25°C to 45°C. It is clear from these data that it takes about 10 hours for the viscosity to reach equilibrium following the temperature jump. Equilibrium viscosities were typically reached more quickly at higher temperatures, with a time of about two hours being required to establish equilibrium at 80°C. The viscosities reported for these ionomers in mixed solvents are all equilibrium viscosities, and were found to be quite reproducible provided sufficient time was allowed for equilibrium to be reached.

Fluids which display increasing viscosity with increasing temperature are obviously quite unusual. The fact that these ionomers in nonpolar-polar solvent mixtures display such unusual viscosity-temperature behavior suggests that they may be useful as viscosity control agents or "thermal thickeners" in applications requiring viscosity to be maintained or increased at high temperatures.

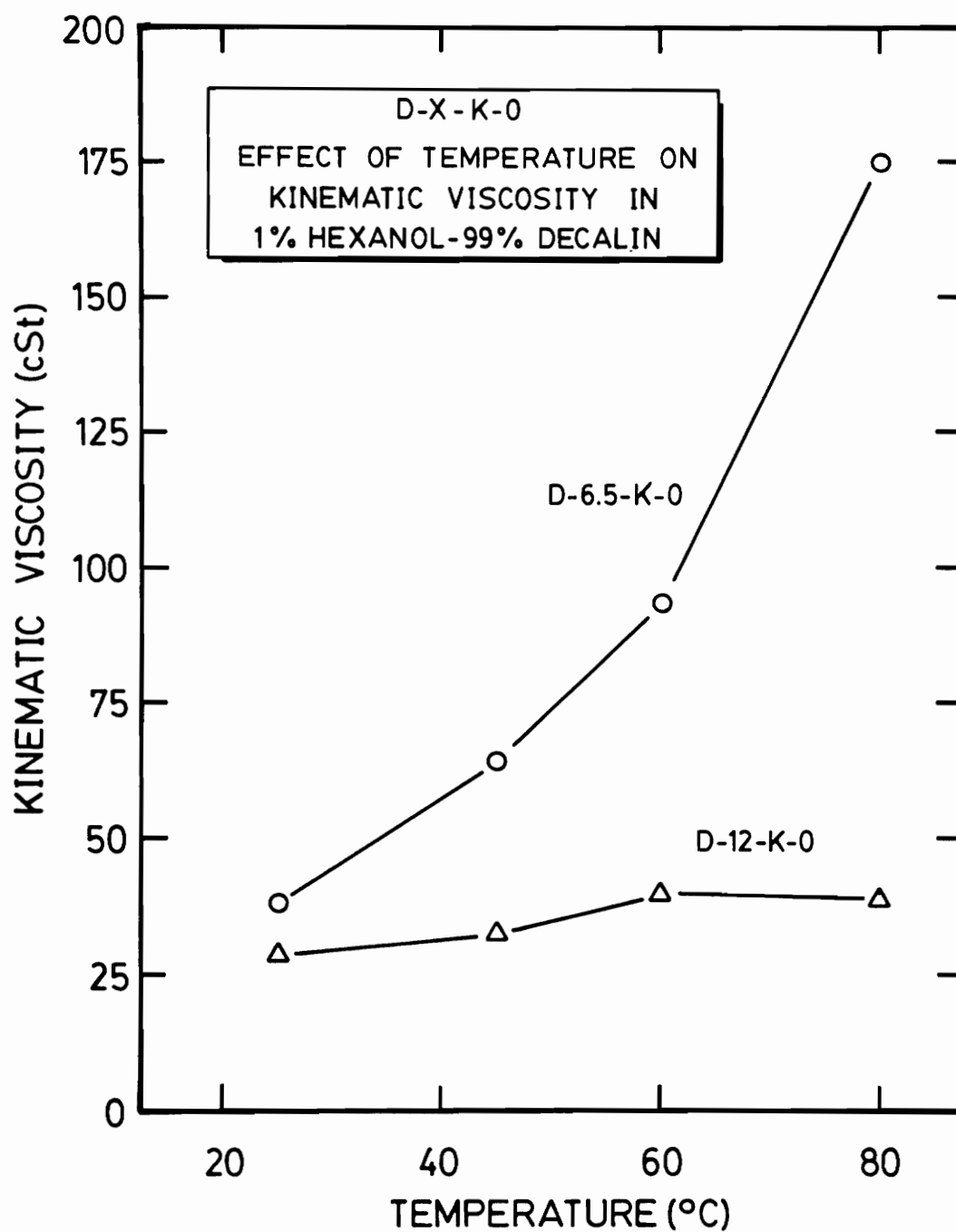


Figure 60. Effect of temperature on kinematic viscosity of D-6.5-K-0 and D-12-K-0 at 2.0 g/dl in 1% hexanol-99% decalin.

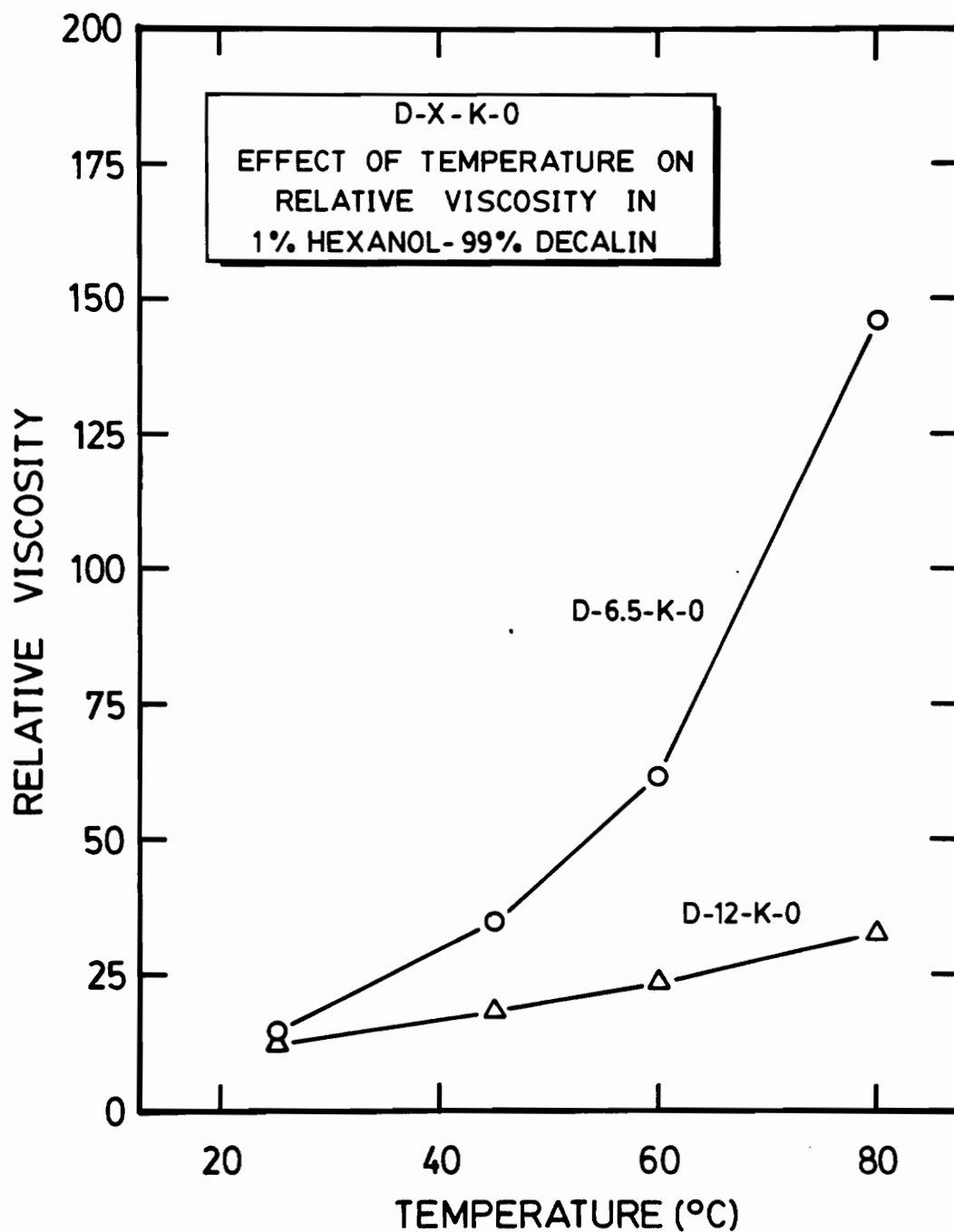


Figure 61. Effect of temperature on relative viscosity of D-6.5-K-0 and D-12-K-0 at 2.0 g/dl in 1%hexanol-99% decalin.

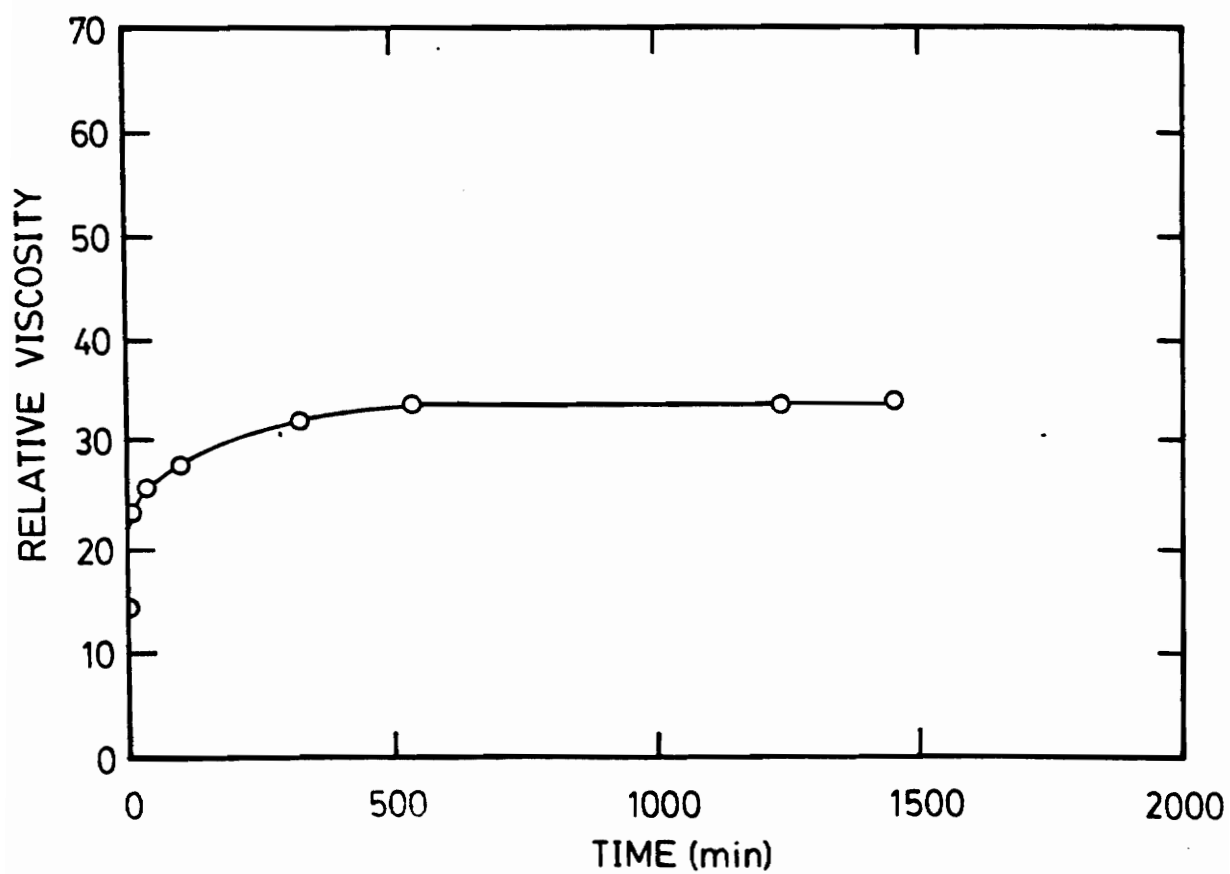


Figure 62. Time dependent relative viscosity of D-6.5-K-0 in 1% hexanol-99% decalin: Following a temperature jump from 25 to 45°C.

Viscoelastic Behavior of Concentrated Solutions

Although the steady shear flow behavior of these ionomer solutions is quite important, viscometric studies give very little information about the dynamics of ionic interactions. In order to study this aspect of the sulfonated polyisobutylene telechelic ionomers in nonpolar solvents, dynamic experiments were conducted on more concentrated solutions in decalin using a Rheometrics Mechanical Spectrometer Model 605 with cone and plate.

Figure 63 shows the storage modulus G' and loss modulus G'' for a 5 g/dl solution of D-12-ZnAc-100 in decalin at 28°C. The striking features of the observed behavior are the fact that G' approaches a slope of 2 and G'' approaches a slope of 1 in the terminal region, but at higher frequencies G' displays a rubbery plateau extending about two decades. According to the Rouse theory for linear flexible random coils [139], the intrinsic moduli are given by

$$[G']_R = \sum_{p=1}^N \frac{\omega^2 \tau_p^2}{(1 + \omega^2 \tau_p^2)} \quad (5.14)$$

and

$$[G'']_R = \sum_{p=1}^N \frac{\omega \tau_p}{(1 + \omega^2 \tau_p^2)} \quad (5.15)$$

where p represents the deformation mode of which there are N and τ_p is the corresponding relaxation time. These equations are derived from the bead-spring model (i.e. atoms in the chain are represented by beads connected by springs) assuming no hydrodynamic interaction among beads. Thus it applies to dilute solutions. At finite concentrations sufficiently small that $[G']_R$ can be approximated by $G'M/cRT = G'/nkT$

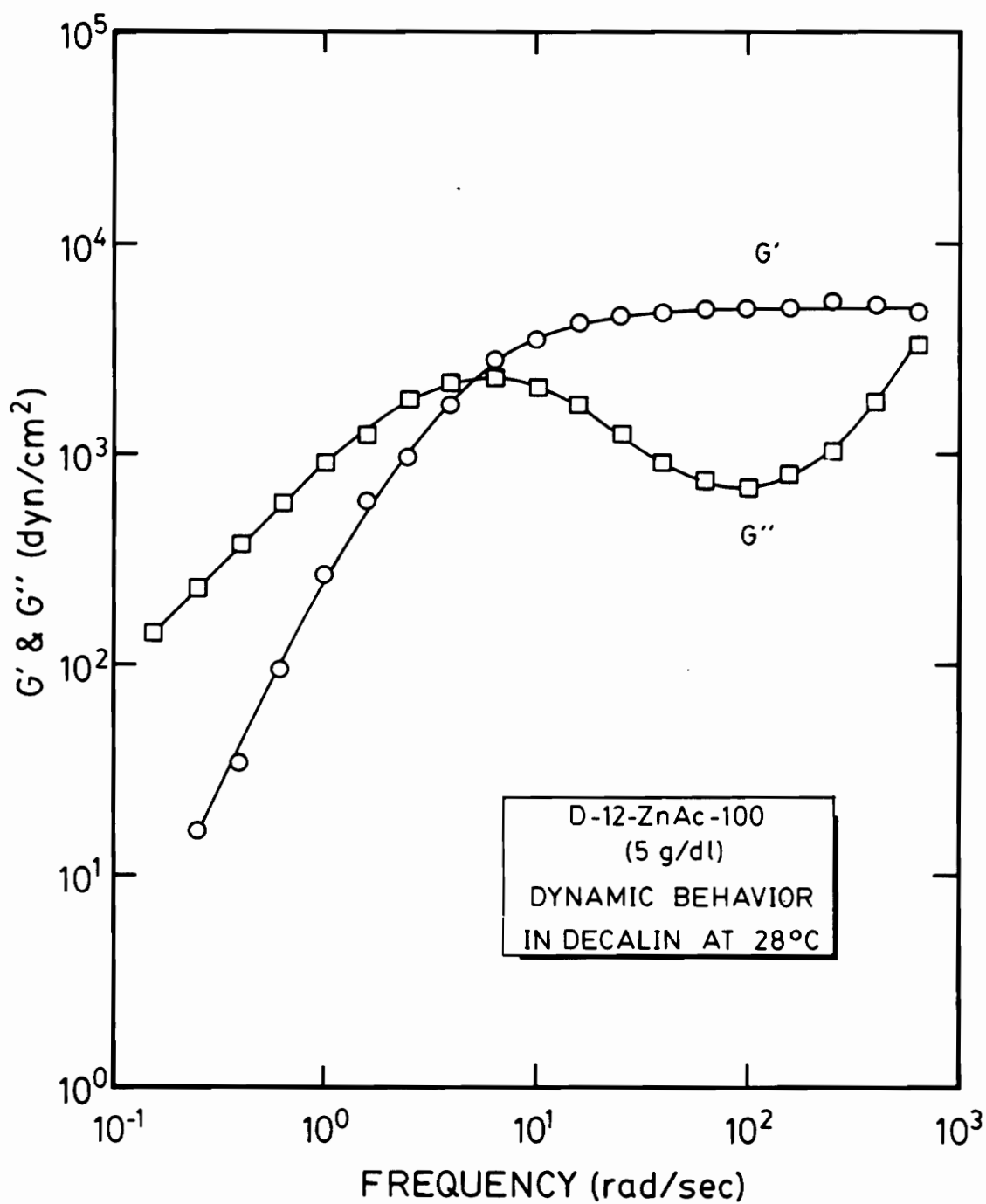


Figure 63. Dynamic behavior of D-12-ZnAc-100 in decalin at 28°C.

where n is the number of polymer molecules per volume, equations (5.14) and (5.15) can be written

$$G' = nkT \sum_{p=1}^N \frac{\omega^2 \tau_p^2}{(1 + \omega^2 \tau_p^2)} \quad (5.16)$$

and

$$G'' = nkT \sum_{p=1}^N \frac{\omega \tau_p}{(1 + \omega^2 \tau_p^2)} \quad (5.17)$$

Thus it is clear that as frequency approaches zero, G' becomes proportional to ω^2 and G'' becomes proportional to ω . On a log-log plot the G' curve should approach a slope of 2 and G'' should approach a slope of 1. Thus the slopes in the terminal region of the G' and G'' curves in Figure 63 are those predicted for a linear viscoelastic fluid. Agarwal and Lundberg [119] observed very similar master curves for a 5 weight percent solution of a zinc-neutralized sulfo-EPDM in a paraffinic oil. The \overline{M}_w of the sulfo-EPDM was about 84000 and the sulfonation level corresponded to about 7 sulfonate groups per molecule distributed randomly along the chain. The limiting slopes for G' and G'' were obtained at low frequencies, and at high frequencies a broad rubbery plateau was observed (see Figure 22a on page 63). The G'' curve for the zinc sulfo-EPDM solution in the plateau region is quite similar to that seen in Figure 63 for the telechelic ionomer solution. In fact, the curves for G' and G'' shown in Figure 63 are qualitatively similar in every respect to those obtained for the zinc sulfo-EPDM solution by Agarwal and Lundberg [119]. What is *very different* about the viscoelastic response of the D-12-ZnAc-100 solution and the zinc sulfo-EPDM solution is that the same diverse responses are observed over very different frequency regions. For the D-12-ZnAc-100 solution these responses are observed in Figure 63 to occur over the frequency range from 10^{-1} to 10^3 rad/s, or four decades. For the zinc sulfo-EPDM solution studied by

Agarwal and Lundberg, the same responses are observed to extend from about 10^{-5} to almost 10^4 rad/s, or nine decades. Also the G' and G'' curves for the zinc sulfo-EPDM are *master curves* obtained by shifting isothermal data obtained over the temperature range from 0°C to 135°C . The data in Figure 63 were obtained at a single temperature. For both solutions G'' shows a distinct peak in the frequency range where G' changes in behavior from a predominantly viscous response to a network response. Both solutions also display another increase in G'' at the high frequency end of the rubbery plateau, suggesting the onset of a transition which would only be observed at higher frequencies or lower temperatures. This anticipated transition is likely to be a transition to more glass-like behavior. The minimum in G'' occurs at about 10^2 rad/s for both solutions.

Figure 64 illustrates the viscoelastic behavior for a 5 g/dl solution of T-11.3-ZnAc-100 in decalin at 27°C . Several differences in behavior between this and the D-12-ZnAc-100 solution are evident. First, G' and G'' do not approach the limiting slopes at low frequency expected for a linear viscoelastic fluid. Second, the onset of the rubbery plateau occurs at least a decade lower for the trifunctional ionomer. Third, the plateau modulus G_N^0 of the T-11.3-ZnAc-100 solution is 1.4×10^4 dyn/cm² while that of the D-12-ZnAc-100 solution is only 5.2×10^3 dyn/cm². Finally, the peak in the loss modulus G'' occurs at a lower frequency for the trifunctional ionomer. Each of these factors is strong evidence that the trifunctional ionomer solution possesses a more extensive network character. This would be expected since each triarm molecule already has a permanent covalent trifunctional junction. Thus only ion pair association is necessary for network formation. For the difunctional ionomer some triplet or higher order associations are required for network formation. These statements are supported by the dilute solution viscosity data which show that the trifunctional ionomer forms a gel at a lower concentration than the difunctional ionomer of a similar molecular weight.

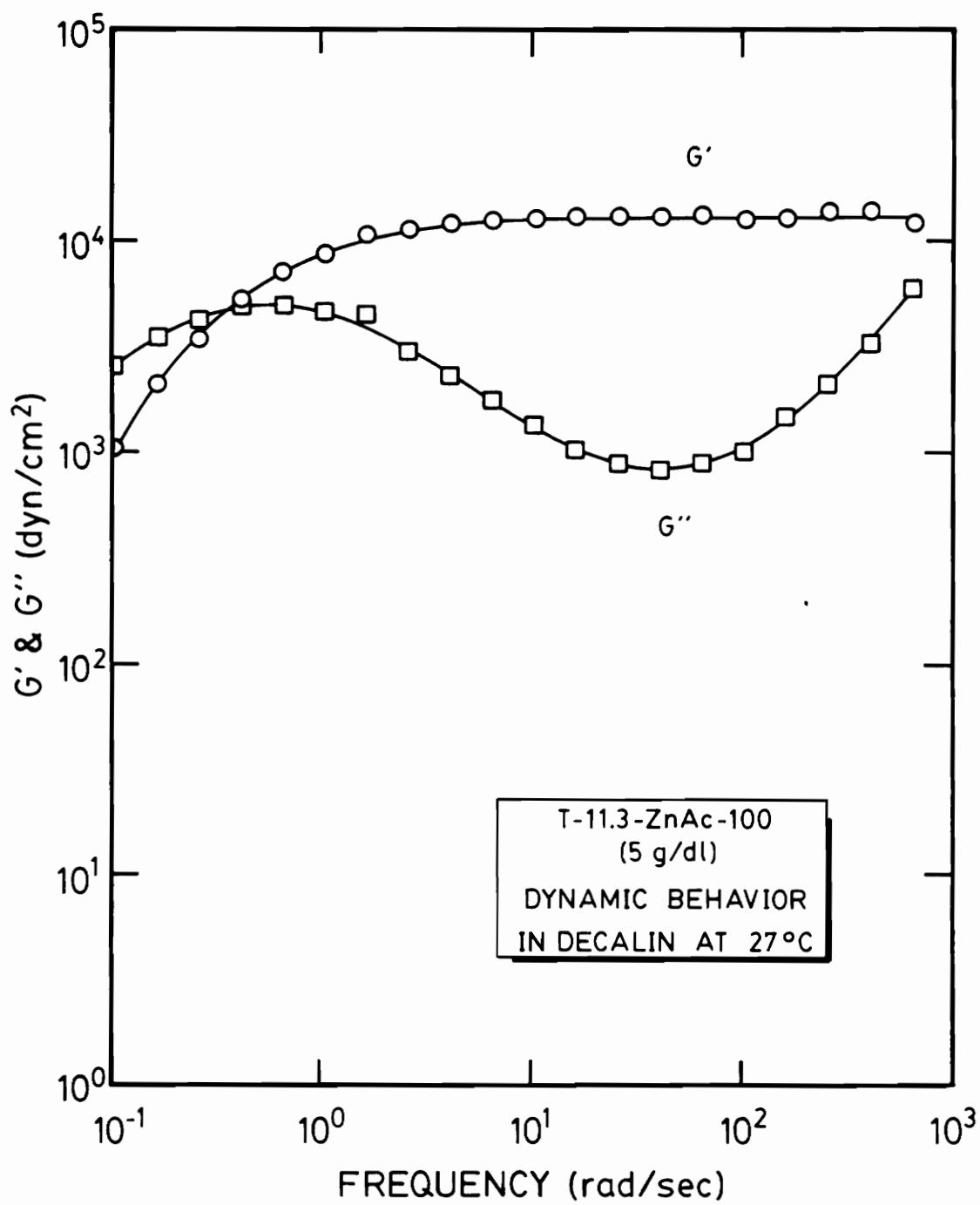


Figure 64. Dynamic behavior of T-11.3-ZnAc-100 in decalin at 27°C.

In Figure 65 the viscoelastic behavior of a solution of high molecular weight ($\overline{M}_w = 1.3 \times 10^6$) linear polyisobutylene at the same concentration of 5 g/dl is shown. The crossover between G' and G'' corresponds approximately to the onset of entanglement coupling [139]. Obviously, below this frequency there are entanglements, but they do not couple as strongly at low frequency and thus do not contribute as much to the elastic response (i.e. by storing energy) as they do at higher frequencies. But it is clear that above this frequency there is not a flat plateau region as is observed for the zinc-neutralized ionomer solutions. Rather, there is only a decrease in the slope of G' . At low frequencies the limiting slopes corresponding to a linear viscoelastic fluid are not even approached by the high molecular weight PIB solution, while these limiting slopes are easily reached by the zinc-neutralized linear telechelic ionomer solution.

Apparently, at low frequencies and low molecular weights the lifetime of the zinc sulfonate association is short compared with the deformation rate, thus allowing the polymer molecules to flow past one another. As the frequency increases, the time scale of the deformation approaches that of the lifetime of the ionic associations. As this occurs the molecules begin to interact more within the time scale of deformation. They are not as free to flow past one another and the slopes of G' and G'' begin to deviate from the limiting slopes in the terminal region. Finally, the time scale of the deformation becomes shorter than the time scale of the average zinc sulfonate association and the solution begins to behave as a network. A distinct plateau in the storage modulus is observed, indicating network-like behavior.

The concept of the Deborah number, introduced by Reiner [140], offers a convenient way to describe this transition from a predominately viscous response to a network response. The Deborah number may be defined as

$$N_{De} = \frac{\lambda_c}{t_s} \quad (5.18)$$

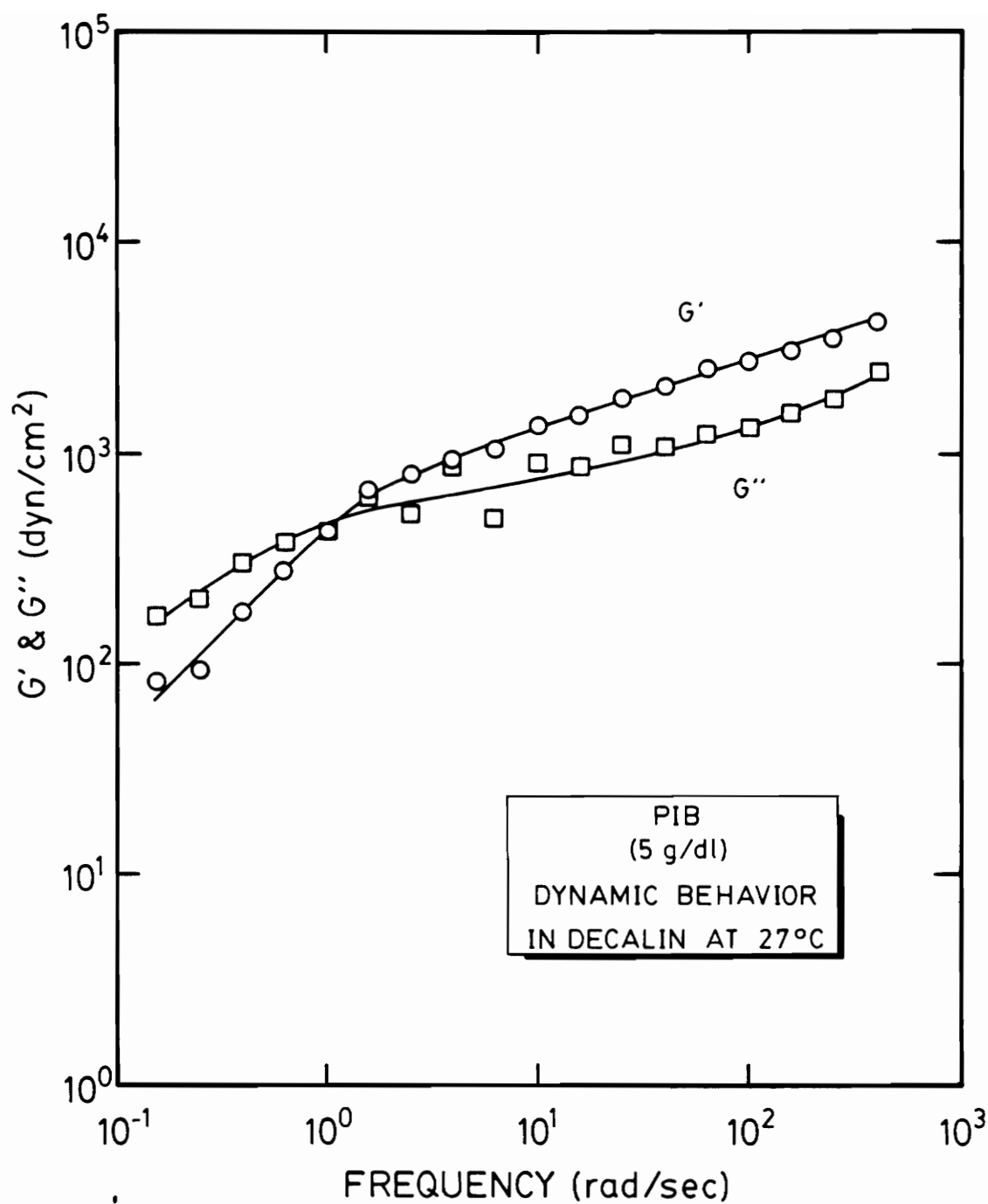


Figure 65. Dynamic behavior of linear polyisobutylene in decalin at 27°C: $\overline{M}_v = 1.3 \times 10^6$.

where λ_c is a characteristic time of the material and t_e is the time scale of the experiment. For the present case λ_c can be defined as an estimate of the average lifetime of an ionic bond and t_e as the inverse frequency, giving

$$N_{De} = \lambda_c \omega \quad (5.19)$$

The fact that ω is in units of rad/s, resulting in units of radians for N_{De} , is not important here. From equation (5.19), high frequencies will result in high Deborah numbers and an elastic response, and low frequencies will result in low Deborah numbers (< 1) and a viscous response. This is the observed behavior.

Figure 66 illustrates the effect of neutralizing cation type upon the storage modulus of the D-6.5 ionomer at a concentration of 5 g/dl in decalin and in the temperature range of 27 to 31°C. (This range of temperatures was the result of the varying room temperature, which could not be controlled.) Clearly, the behavior of solutions of D-6.5 stoichiometrically neutralized with K^+ , Ca^{2+} , and Ce^{3+} is very similar, but there is no trend with the valence of the cation. The rubbery plateau is seen to persist over essentially all four experimentally accessible decades of frequency, with a slight decrease in G' at the lowest frequencies. Thus these solutions display network behavior over the entire frequency range. The solution with 100% excess zinc acetate displays a predominantly viscous flow response at low frequencies, as described earlier, and is thus very different from the other solutions. As has been discussed before, the zinc sulfonate interactions are much weaker than those of the other cations due to the less ionic, more coordinative character of the zinc bonds. The fact that the plateau modulus G_N^0 of D-6.5-K-0, D-6.5-Ca-0, and D-6.5-Ce-0 are all very similar suggests that the network and crosslink densities are all similar despite the variation in cation valence.

Two of the curves in Figure 67 show the effect of molecular weight for the linear difunctional species stoichiometrically neutralized with KOH and at a concentration of

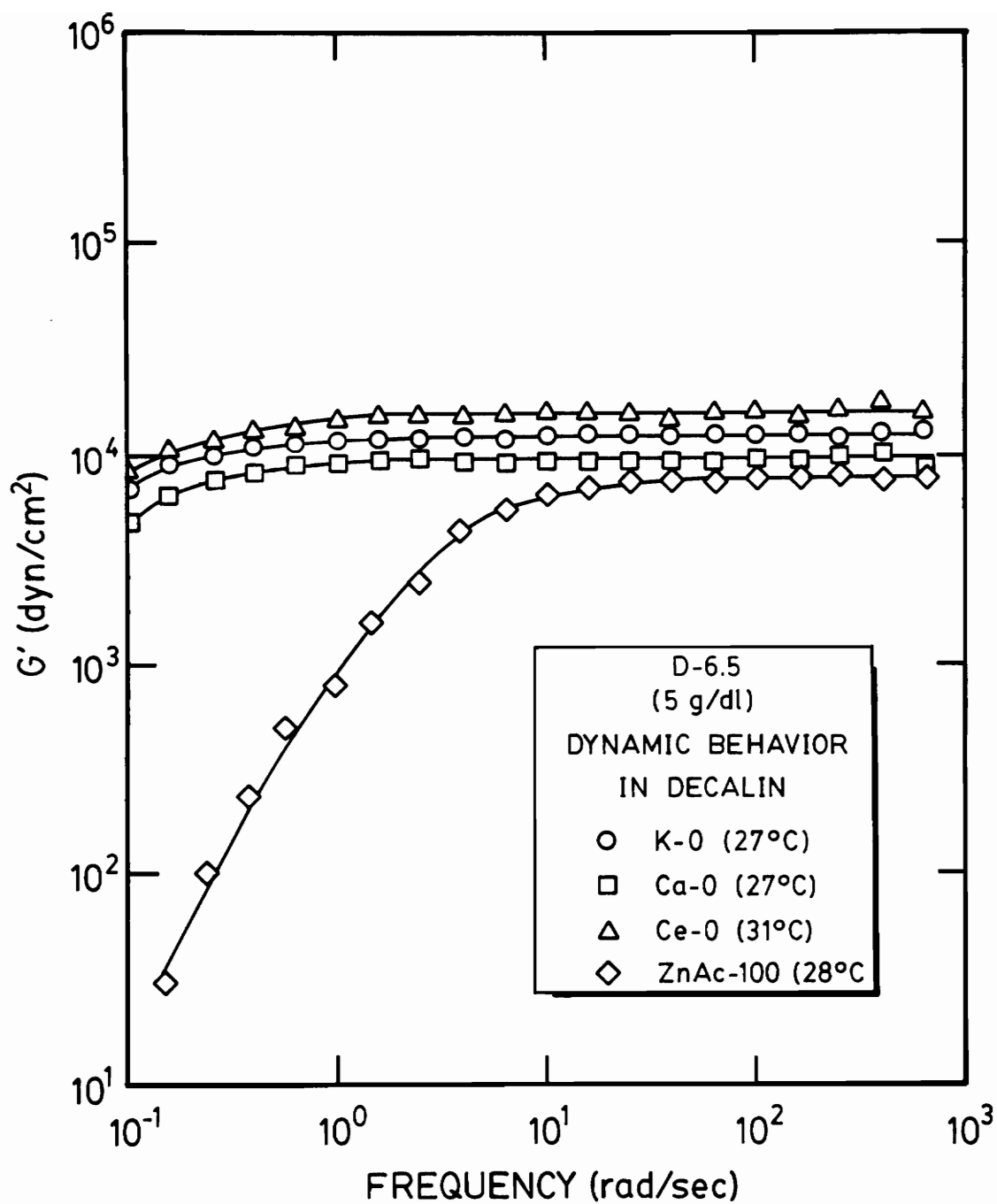


Figure 66. Effect of cation type upon G' of D-6.5 ionomer in decalin at 5 g/dl.

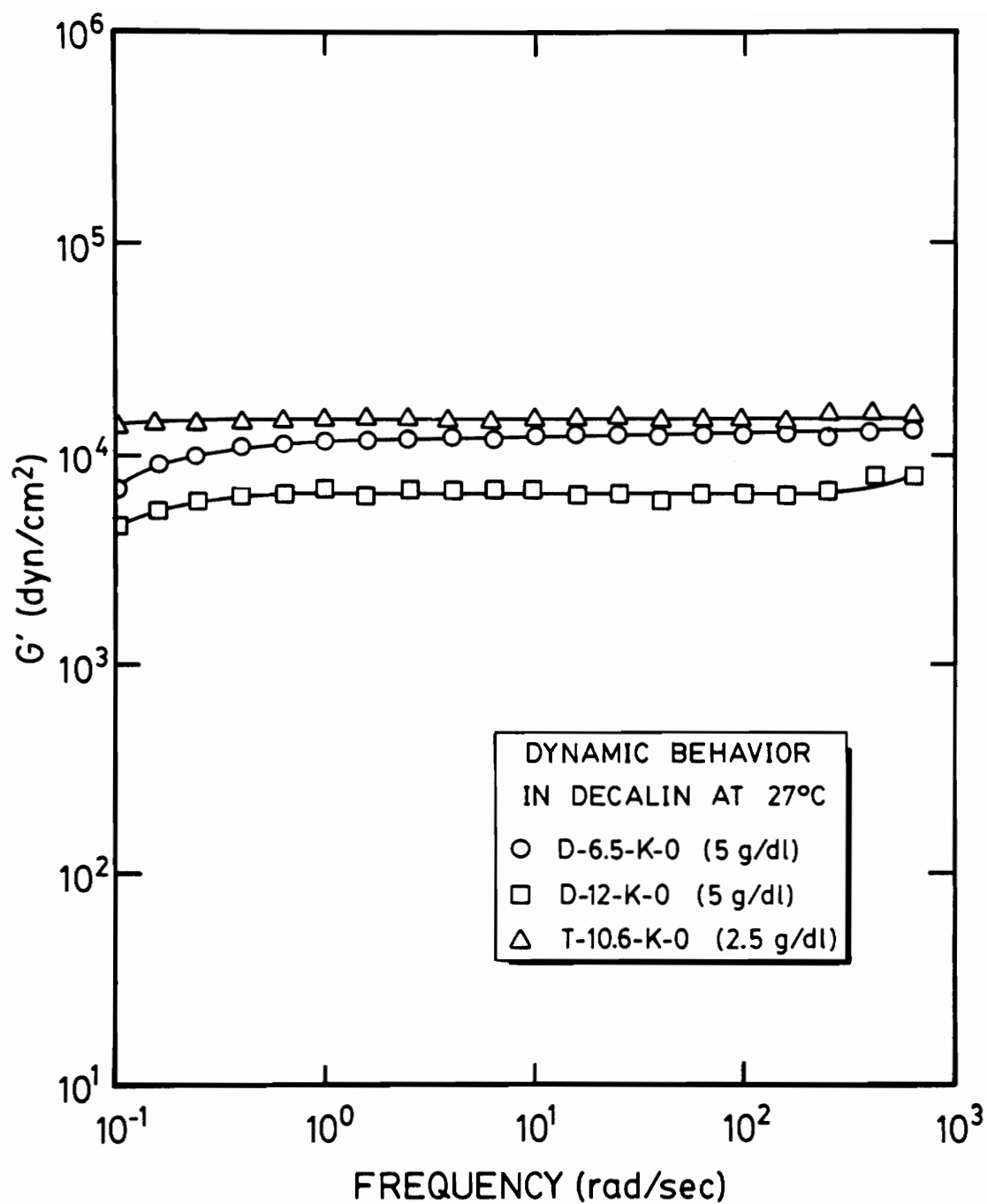


Figure 67. Effect of molecular weight upon dynamic behavior of linear difunctional ionomers in decalin at 5 g/dl.

5 g/dl in decalin. The plateau modulus of the D-6.5-K-0 solution is substantially higher than that of the D-12-K-0 solution over the entire range of frequencies. This supports the gelation experiments which showed that D-6.5 gels at a lower concentration than D-12. Again, both findings indicate that the D-6.5 material forms a network with a higher ionic crosslink density than the D-12 material. It is interesting to compare the G' of these two solutions with that of the solution of T-10.6-K-0 at exactly half the concentration, i.e. 2.5 g/dl. The T-10.6-K-0 solution displays about the same plateau modulus as the D-6.5-K-0 solution even though it is only half as concentrated. This is another indication that the trifunctional molecules find it much easier to form a network than the difunctional molecules.

The effect of molecular weight upon the storage modulus G' of the trifunctional species stoichiometrically neutralized with KOH is illustrated in Figure 68 for 2.5 g/dl solutions in decalin between 27 and 31°C. The plateau modulus is highest for the T-10.6-K-0 solution due to its lower molecular weight and thus higher crosslink density. Upon increasing \overline{M}_n from 10600 to 19000, G_N^0 is observed to drop from 1.5×10^4 dyn/cm² to 4.7×10^3 dyn/cm². This large decrease in G_N^0 is due to the decrease in crosslink density as molecular weight is increased. Increasing the \overline{M}_n from 19000 to 34000 results in only a slight reduction in the plateau modulus, G_N^0 - from 4.7×10^3 to 3.8×10^3 dyn/cm². This small decrease in G_N^0 can be attributed to the onset of entanglement coupling as \overline{M}_n is increased from 19000 to 34000. Thus, while the crosslinks which determine G_N^0 for the T-10.6 and T-19 solutions are primarily the result of ionic associations, the crosslinks which determine G_N^0 for the T-34 solution are the result of both ionic associations and entanglements.

Figure 69 shows the effect of concentration on the behavior of D-6.5-K-0 in decalin at 27-31°C. The plateau modulus G_N^0 is observed to increase with increasing concentration as expected. Agarwal and Lundberg [119] have found that unsulfonated EPDM

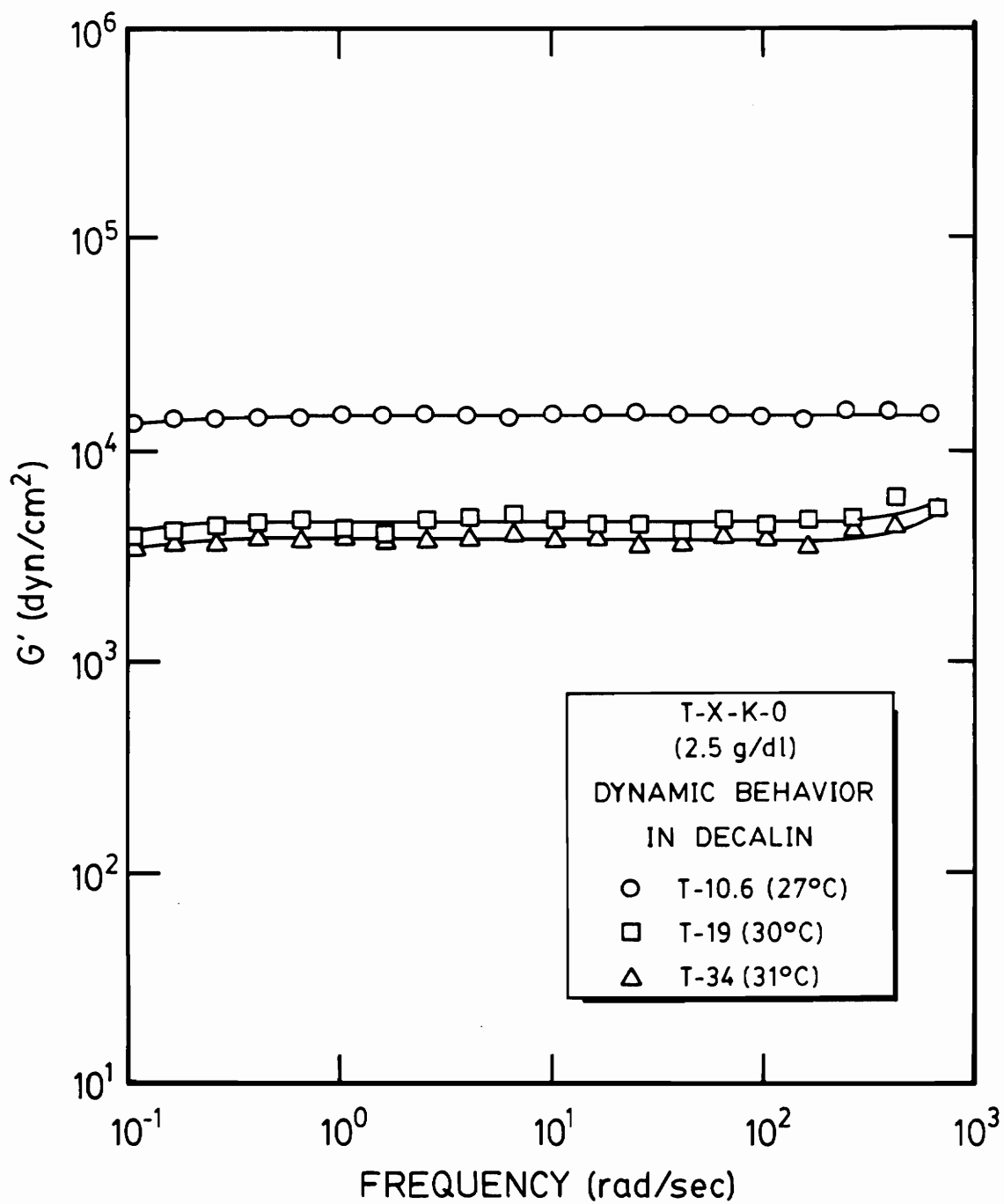


Figure 68. Effect of molecular weight upon G' of three-arm star trifunctional species in decalin at 2.5 g/dl.

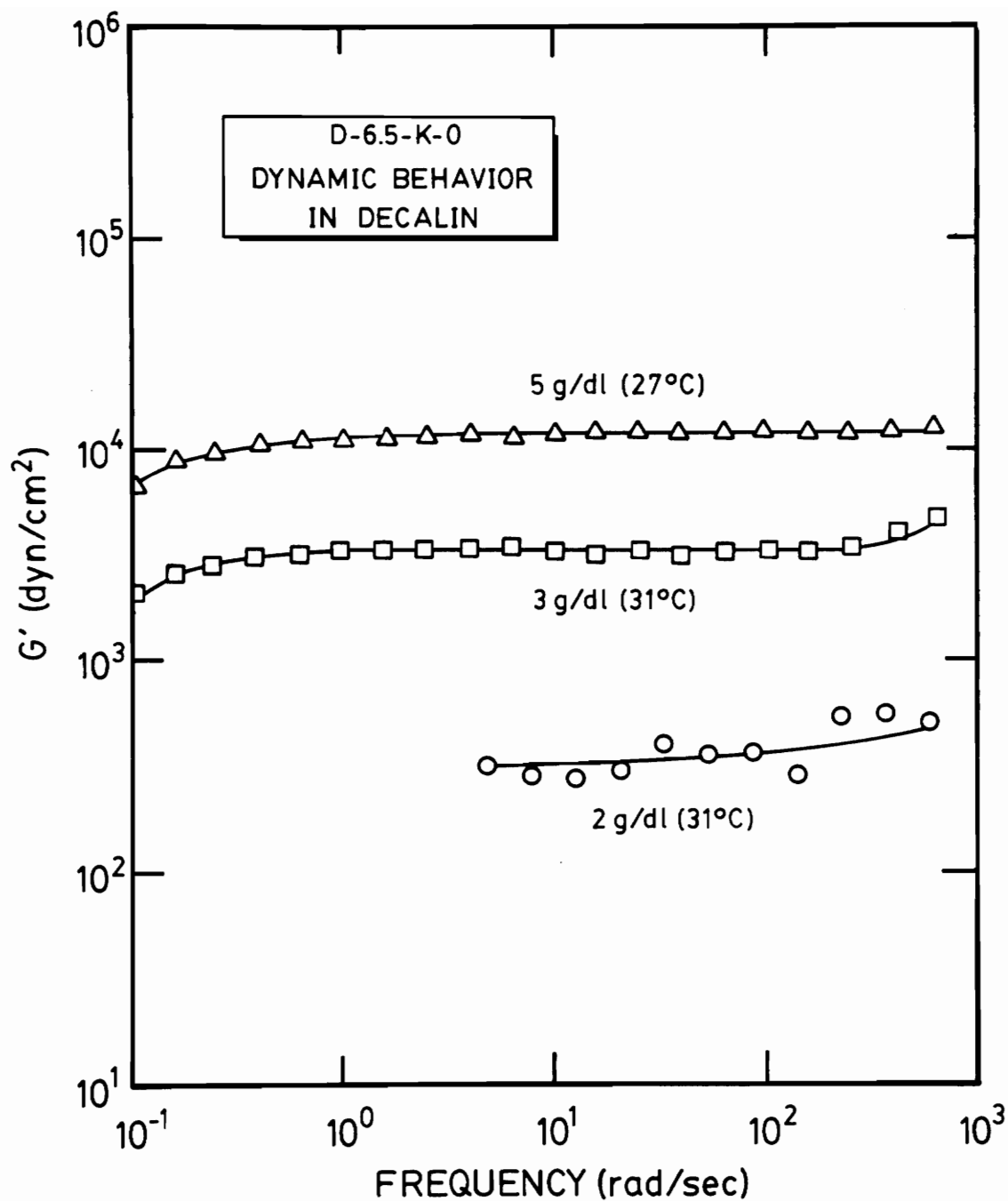


Figure 69. Effect of concentration upon G' of D-6.5-K-0 in decalin at 27-31°C.

solutions display a G_N^0 which is proportional to c^2 , the square of the concentration, while solutions of sulfonated EPDM show a stronger dependency on concentration, i.e. $G_N^0 \propto c^{2.5}$. The values of G_N^0 from Figure 69 are plotted in Figure 70 in terms of $\log G_N^0$ vs. $\log c$. Since the 2 g/dl solution is near the gelation point and not well into the gel region, a line was drawn only between the points for the 3 and 5 g/dl solutions. Although the data is obviously very limited, the slope of the line is 2.5 - the same as that found by Agarwal and Lundberg for their sulfonated EPDM solutions. Similar data on D-12-K-0 solutions at concentrations of 5 and 10 g/dl revealed a $c^{2.15}$ dependency. Clearly, additional data must be obtained to accurately establish the dependence of G_N^0 upon concentration. Limitations on the present study were imposed by the lack of sufficient amounts of material.

The effects of temperature upon the viscoelastic behavior of a 10 g/dl solution of D-12-K-0 in decalin are shown in Figure 71 and 72. Two effects of temperature are obvious. First, the terminal region is shifted to higher frequencies by increasing the temperature. This is an expected result. However, the large increase in the plateau modulus G_N^0 with increasing temperature was not expected. Certainly, some increase in G_N^0 would be expected due to the temperature effects of rubber elasticity, but not to the degree observed. Figures 73 and 74 show that somewhat similar behavior occurs for the T-10.6-K-0 ionomer in decalin at a concentration of 2.5 g/dl. The terminal region shifts to higher frequencies while G_N^0 shows a general increase with temperature.

While the breadth of the rubbery plateau is related to the lifetime of the ionic associations [119], the rubbery plateau modulus is related to the crosslink density. Thus while increasing the temperature shortens the lifetime of the ionic associations, it seems to be increasing the crosslink density of the ionomer in solution. This may be due to the increased Brownian motion of the chains which would increase the probability of an ionic group making contact with another ionic group and forming an ionic crosslink.

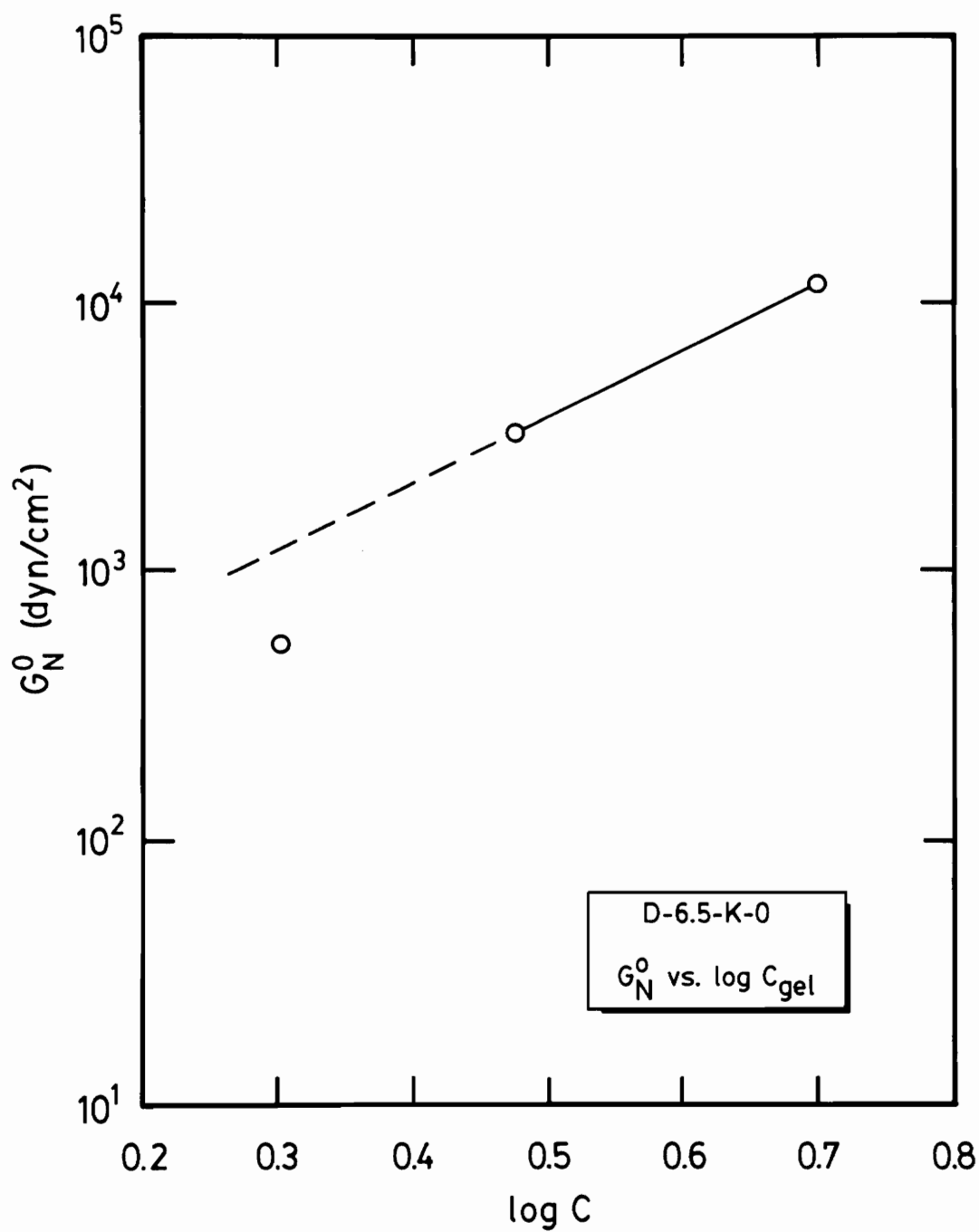


Figure 70. Plot of log of plateau modulus vs. log of concentration for D-6.5-K-0 in decalin.

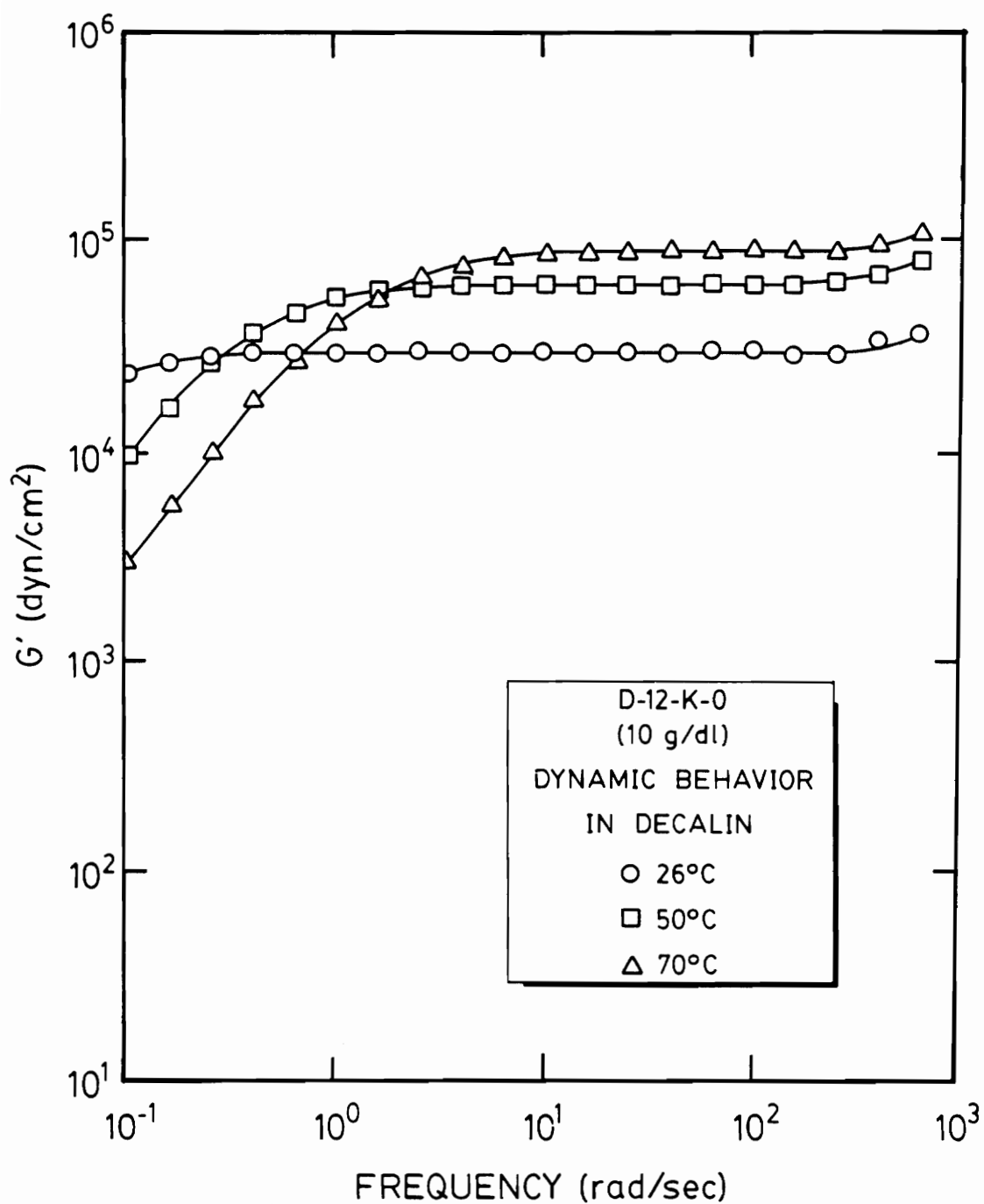


Figure 71. Effect of temperature upon G' of D-12-K-0 in decalin at 10 g/dl.

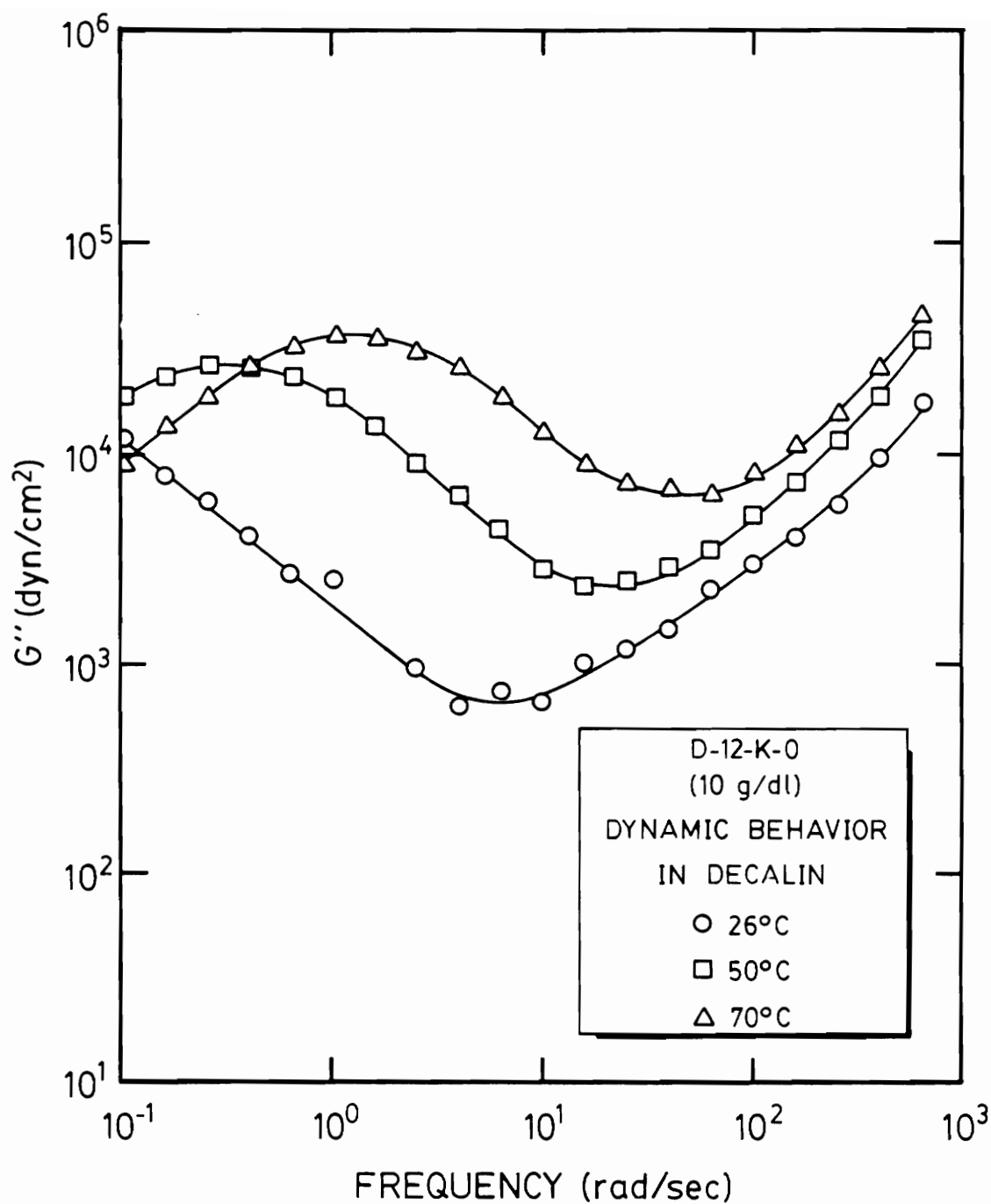


Figure 72. Effect of temperature upon G'' of D-12-K-0 in decalin at 10 g/dl.

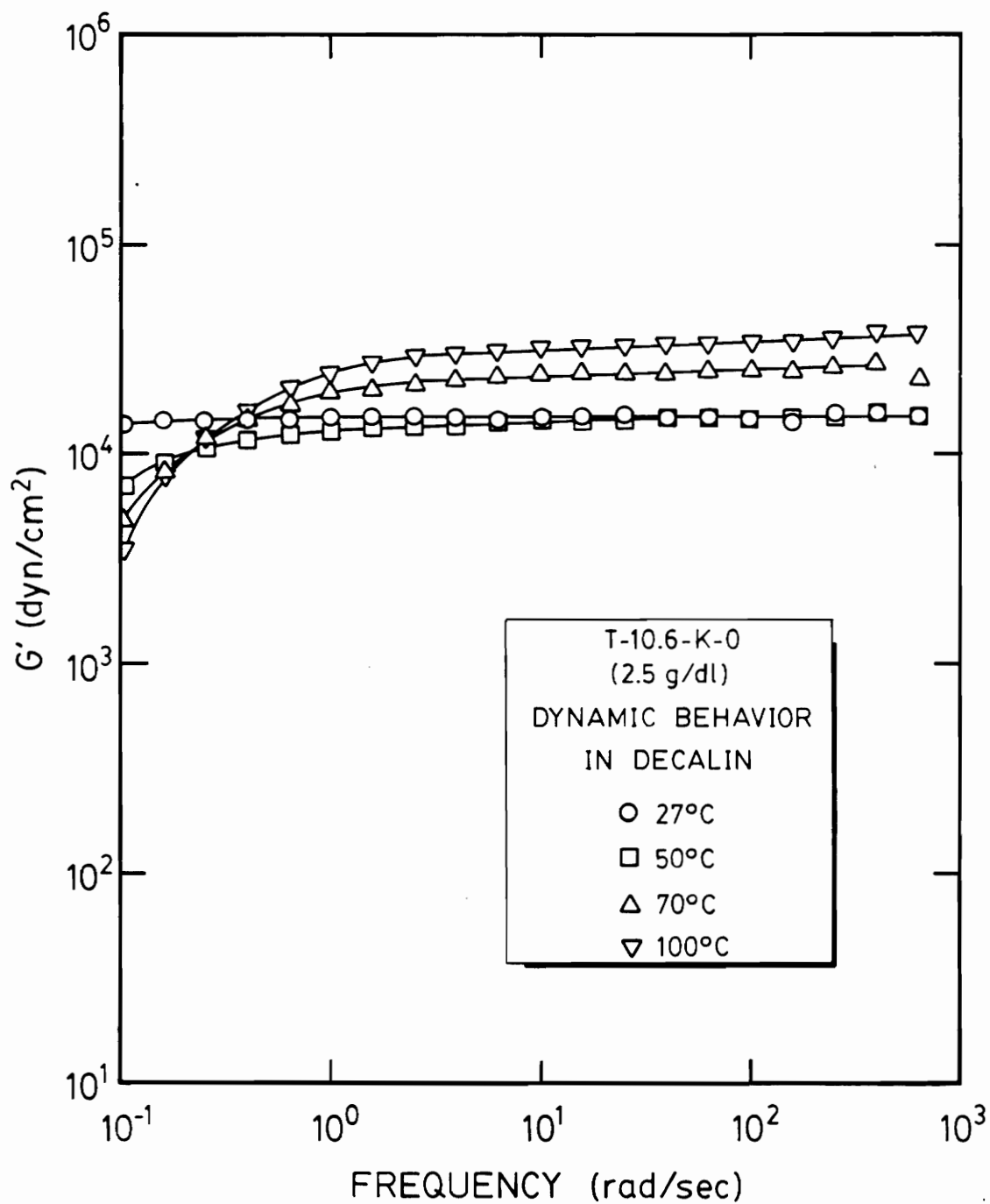


Figure 73. Effect of temperature upon G' of T-10.6-K-0 in decalin at 2.5 g/dl.

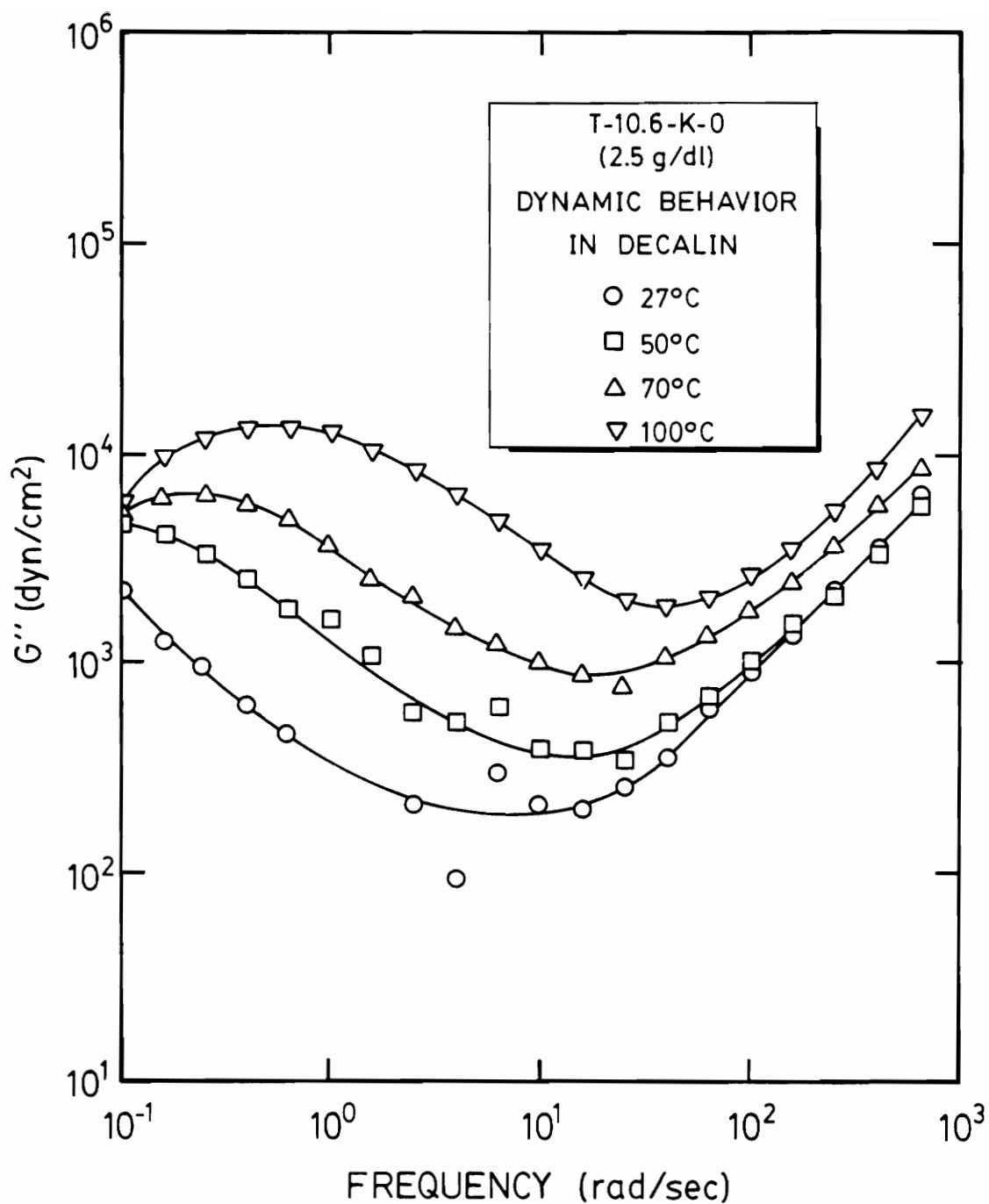


Figure 74. Effect of temperature upon G'' of T-10.6-K-0 in decalin at 2.5 g/dl.

But this increase in plateau modulus with temperature was not observed by Agarwal and Lundberg [119,120] for the sulfonated EPDM's. These polymers, however, had ionic groups randomly distributed along the chain. The mobility of ionic groups along the chain would not be expected to increase as much as terminal ionic groups and thus may not affect the crosslink density significantly.

In order to further investigate the viscoelastic behavior of solutions of these ionomers in a nonpolar solvent, experiments were conducted on solutions of D-6.5-K-0 and T-34-K-0 in 100N oil - the same paraffinic oil utilized by Agarwal and Lundberg in their studies of sulfonated EPDM solutions. D-6.5-K-0 was selected because it possesses the highest concentration of ionic groups and does not have a permanent covalent network junction point. Its behavior is therefore dominated by ionic interactions. On the other hand, T-34-K-0 was selected because it has the lowest ionic content and it does have a permanent network junction point.

One difference between 100N oil and decalin that became obvious at an early stage is that the kinetics of the dissolution process are much slower in 100N oil than in decalin. This is likely due to the long chain nature of the 100N oil which would be expected to reduce the mobility of the ionomer and thus retard dissolution. Preparation of solutions in decalin normally required 2-3 days, while preparation of solutions in 100N oil often required 2-3 weeks.

Figures 75, 76, 77, and 78 show the dynamic behavior of D-6.5-K-0 in 100N oil at a concentration of 10 g/dl and at temperatures of 31, 50, 70, and 100°C, respectively. Composite plots of G' and G'' are shown in Figures 79 and 80, respectively. In Figure 75 it is seen that the terminal slopes of 2 for G' and 1 for G'' are reached. It may be recalled that for D-6.5-K-0 in decalin, and at 5 g/dl instead of 10 g/dl, the storage modulus was essentially constant over all four decades. Apparently, the mobility of the chain ends in 100N oil is so much lower than in decalin that the ionic groups have a

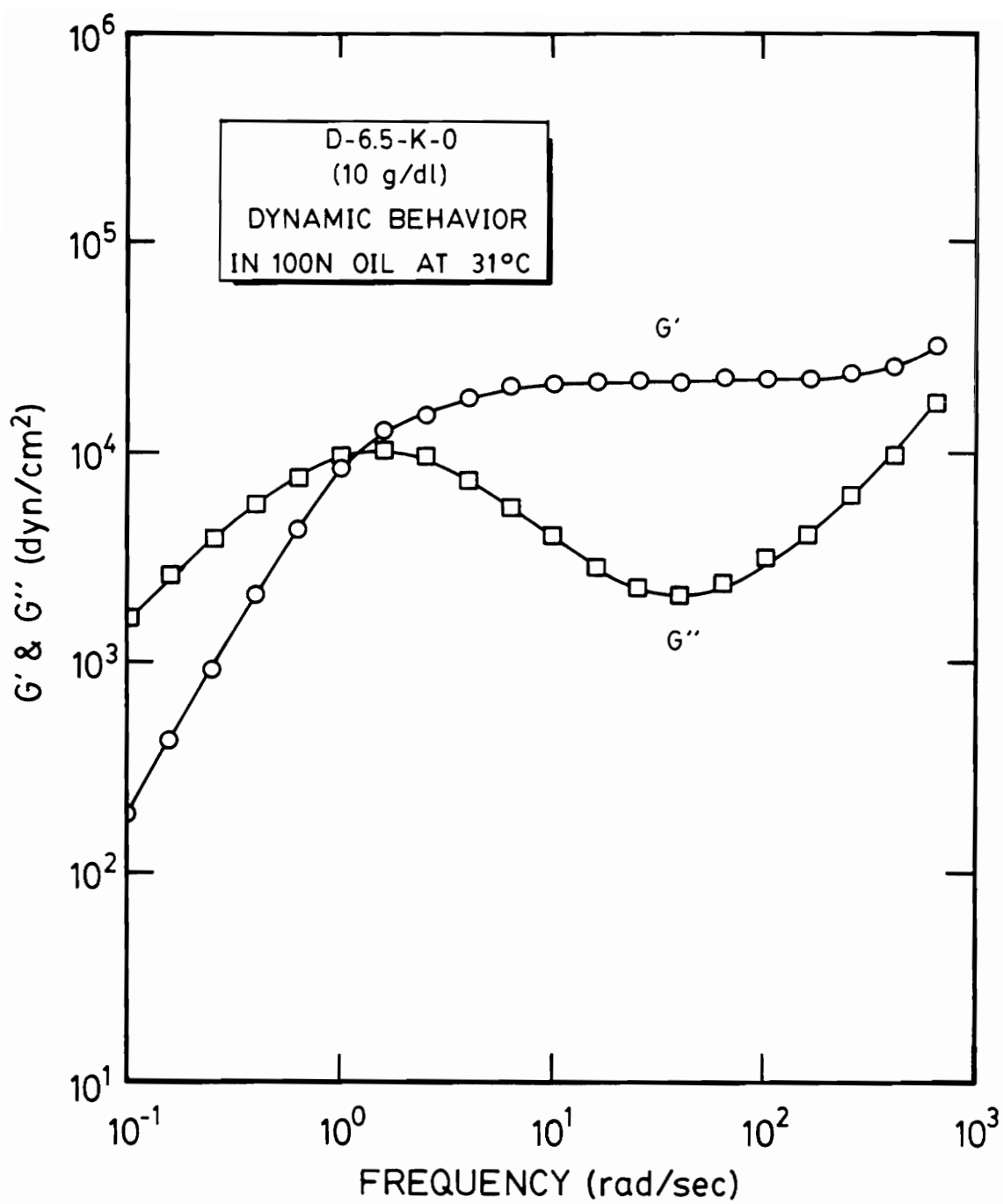


Figure 75. Dynamic behavior of D-6.5-K-0 in 100N oil (10 g/dl) at 31°C.

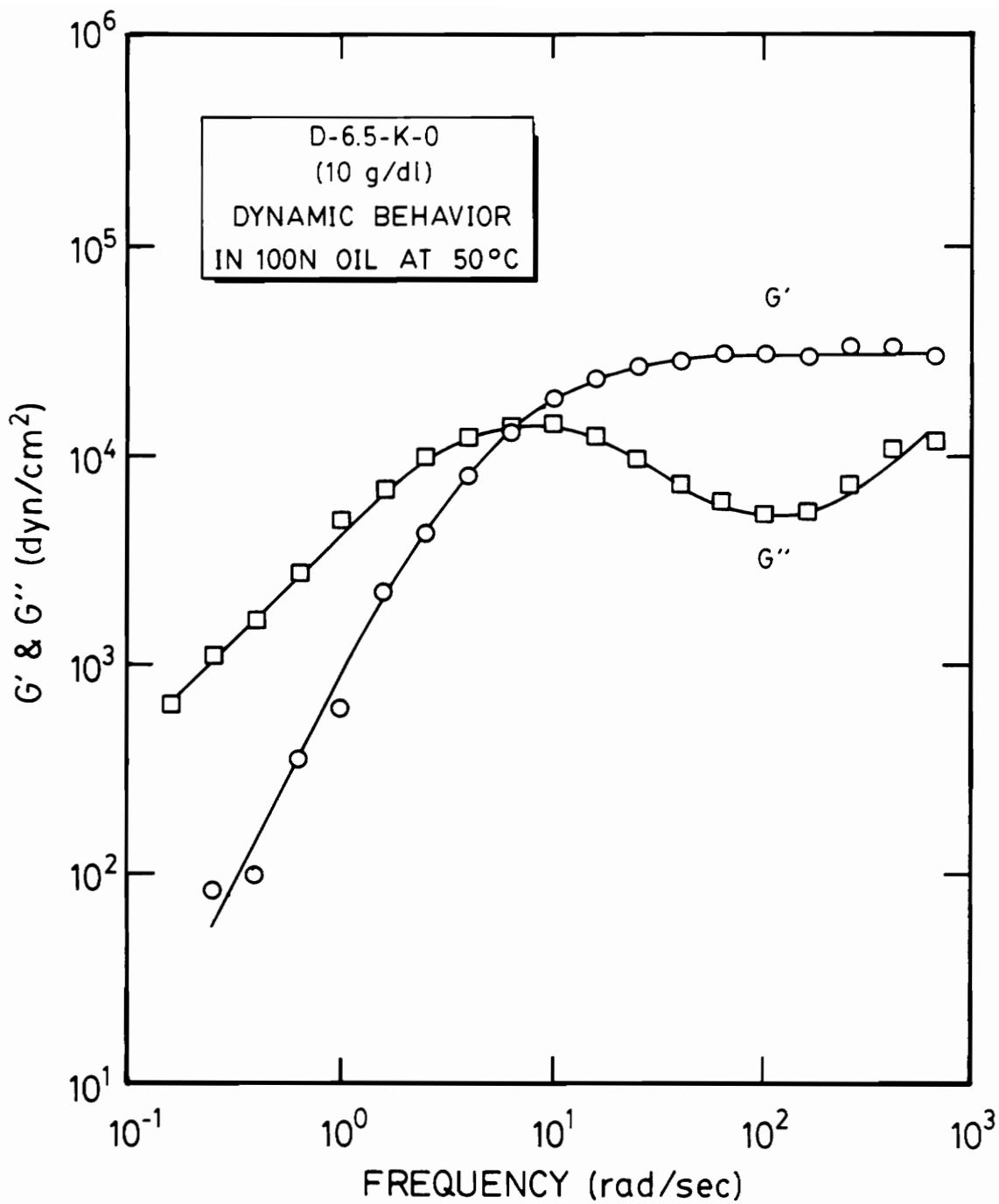


Figure 76. Dynamic behavior of D-6.5-K-0 in 100N oil (10 g/dl) at 50°C.

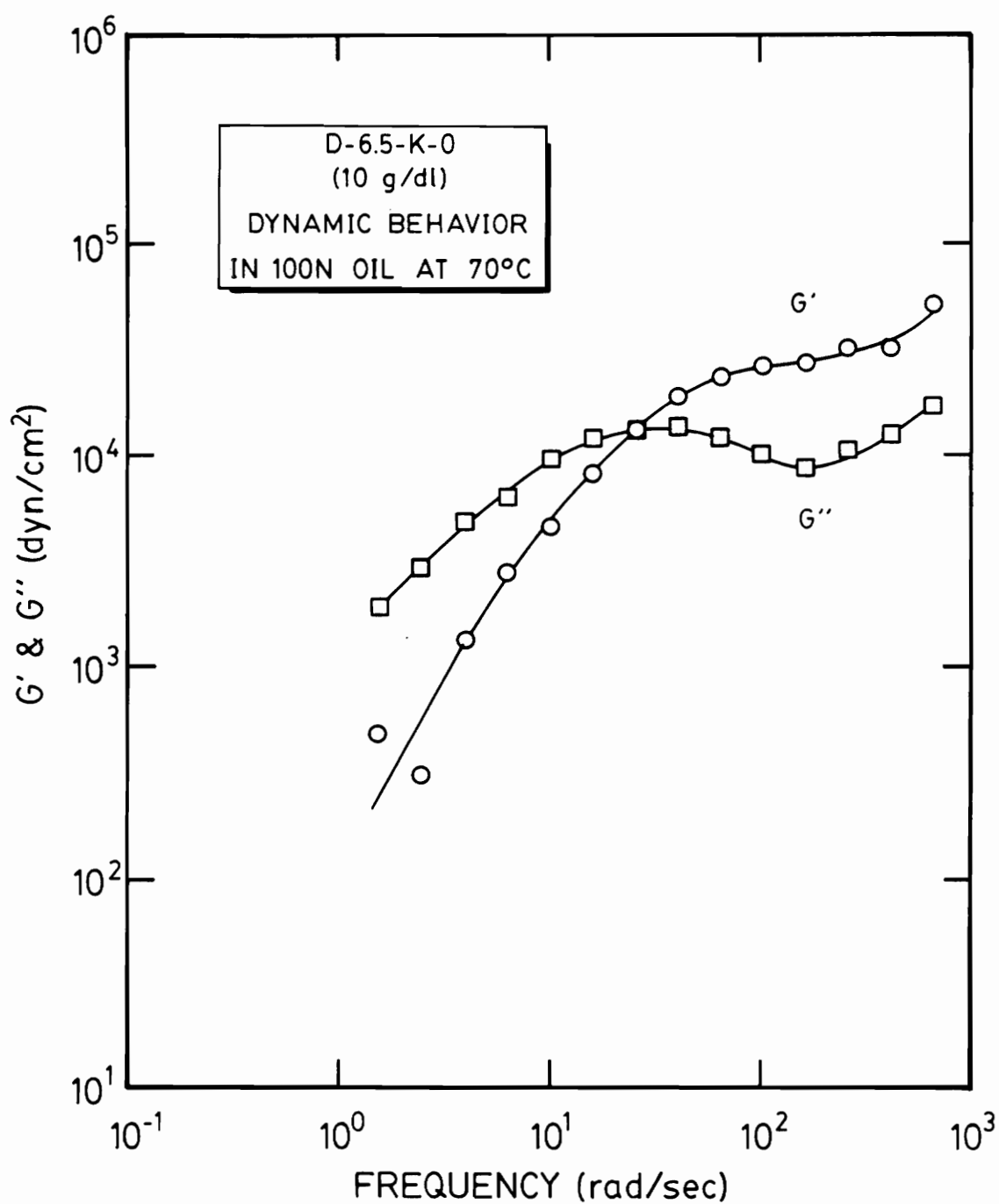


Figure 77. Dynamic behavior of D-6.5-K-0 in 100N oil (10 g/dl) at 70°C.

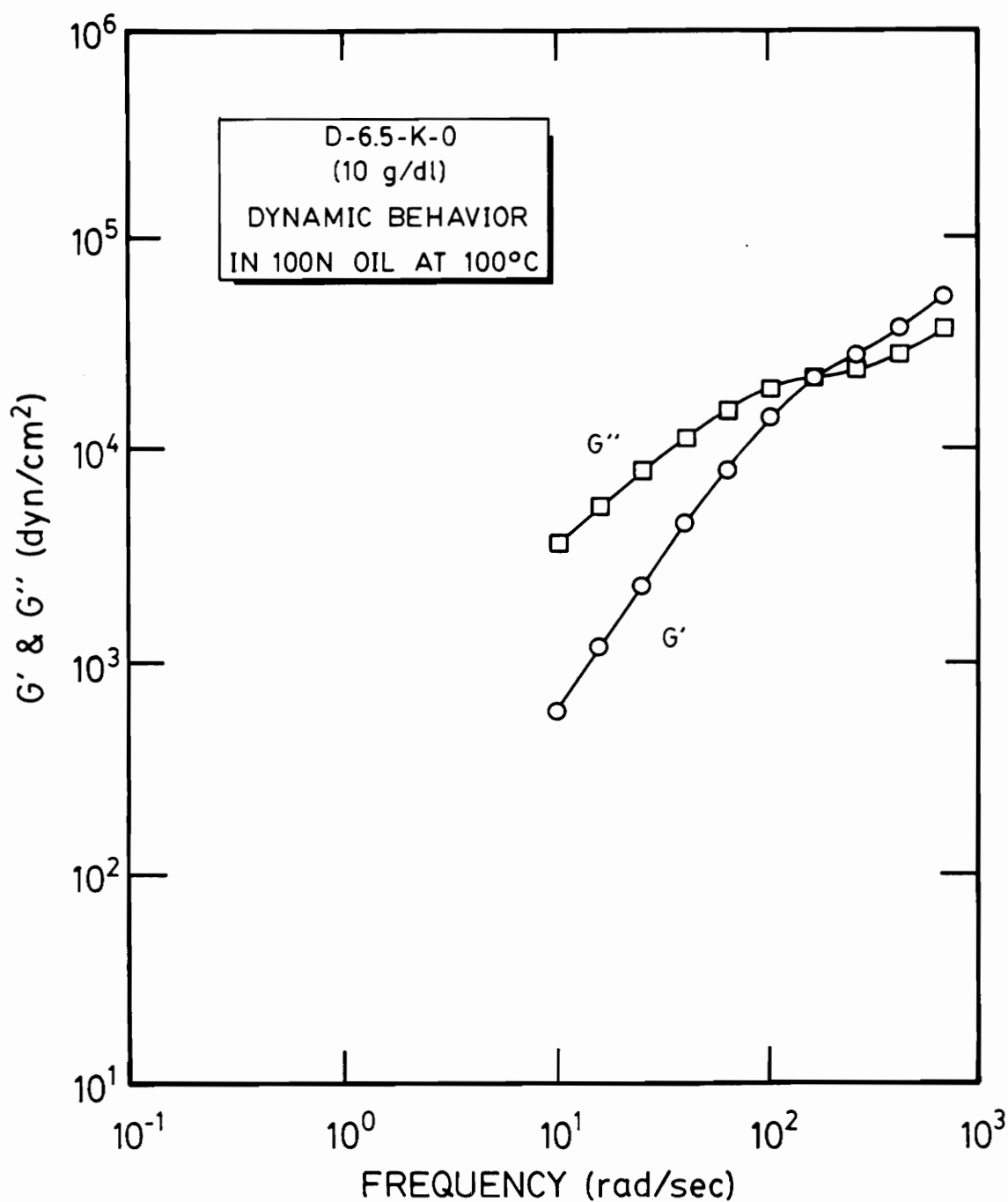


Figure 78. Dynamic behavior of D-6.5-K-0 in 100N oil (10 g/dl) at 100°C.

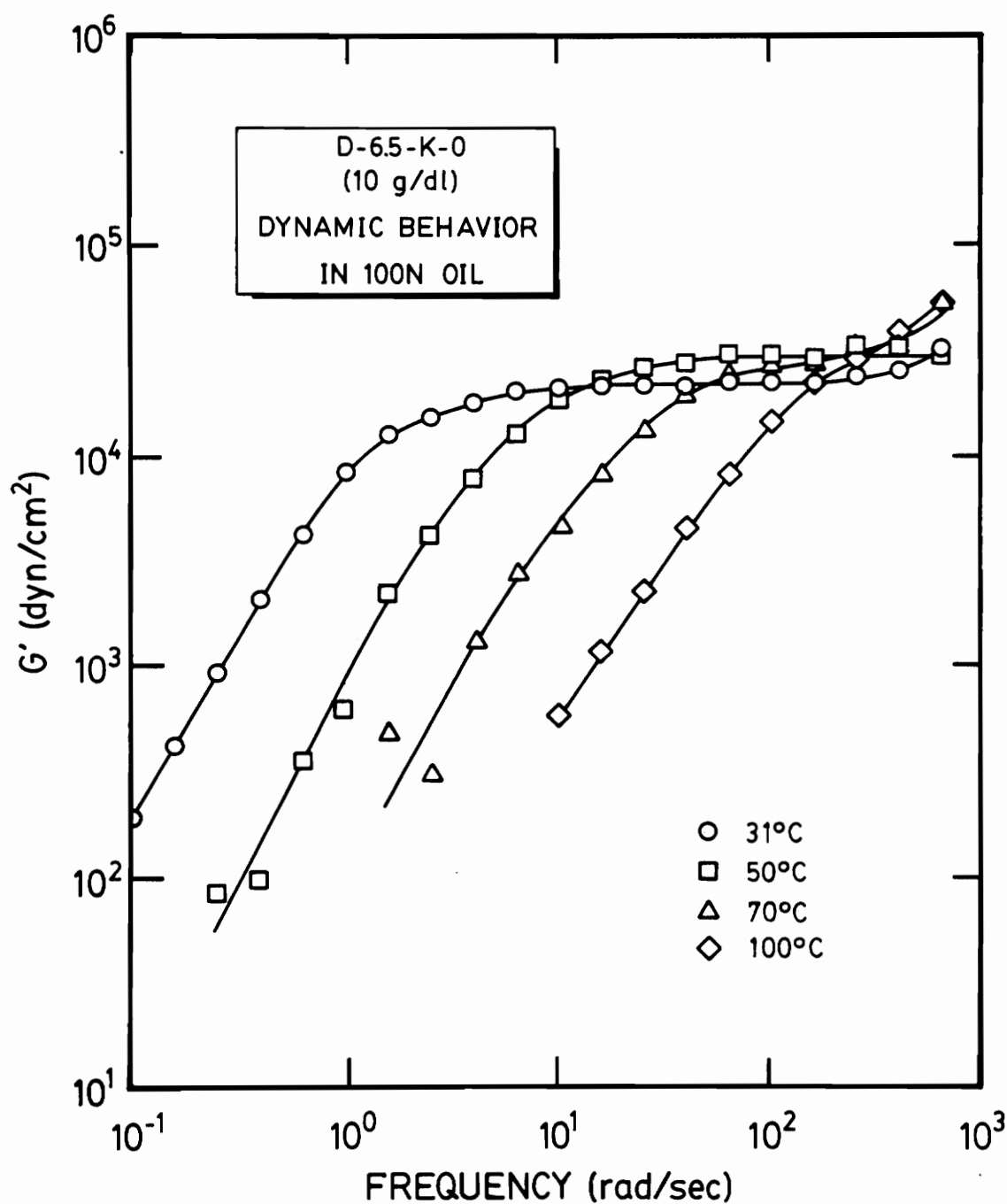


Figure 79. Effect of temperature upon G' of D-6.5-K-0 in 100N oil (10 g/dl).

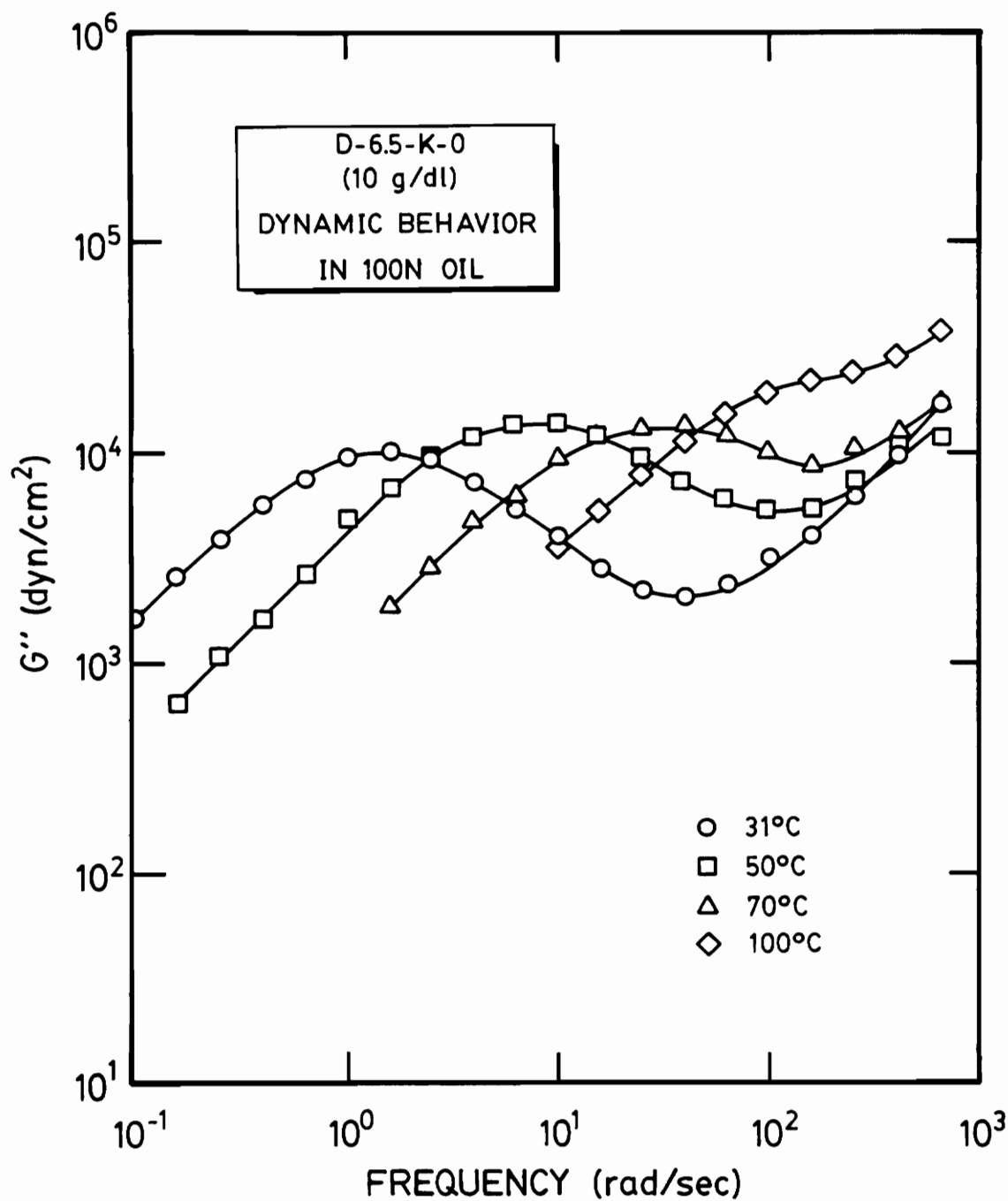


Figure 80. Effect of temperature upon G'' of D-6.5-K-0 in 100N oil (10 g/dl).

much more difficult time finding other ionic groups with which to associate. This both shortens the plateau region and reduces the plateau modulus. Increasing the temperature further reduces the breadth of the plateau by shortening the lifetime of the ionic interactions. An increase in G_N^0 is observed when the temperature is raised from 31 to 50°C, similar to that observed for the decalin solutions. However, no further increases in G_N^0 were observed. When the temperature reaches 100°C, a clear rubbery plateau is no longer observed - just an inflection in the G' curve. Nor is a peak in the G'' curve, which indicates a transition in behavior, now observed.

The composite plots of G' and G'' in Figure 79 and 80 clearly show the shifting of the terminal region to higher frequencies. It is quite apparent, particularly from the G'' curves, that these curves cannot be shifted to superpose and the solution is therefore thermorheologically complex. In fact, while the terminal region shifts toward the right with increasing temperature, the high frequency transition to glass-like behavior, which is indicated by the increase in both G' and G'' , seems to remain at essentially the same frequency. Even though the curves are not superposable, it was considered of interest to determine shift factors for the temperature dependence of the terminal flow region. The onset of the terminal flow region was arbitrarily defined to occur at the frequency where G' is 10^4 dyn/cm². A reference temperature of 31°C was selected and a shift factor a_T was determined for each of the other three curves so that shifting would cause these curves to intersect the 31°C curve at a G' of 10^4 dyn/cm². These shift factors are plotted in Figure 81 in terms of $\log a_T$ vs. $1/T$. Clearly, the relationship is linear, indicating an Arrhenius temperature dependence for the onset of the terminal flow region. Of course, this data was obtained over a limited temperature range and should not be extrapolated far beyond this region. Again, one may use the concept of the Deborah number, $N_{De} = \frac{\lambda_e}{t_r}$, to describe the temperature dependence of the transition from viscous to elastic behavior. For high Deborah numbers the response is elastic and for

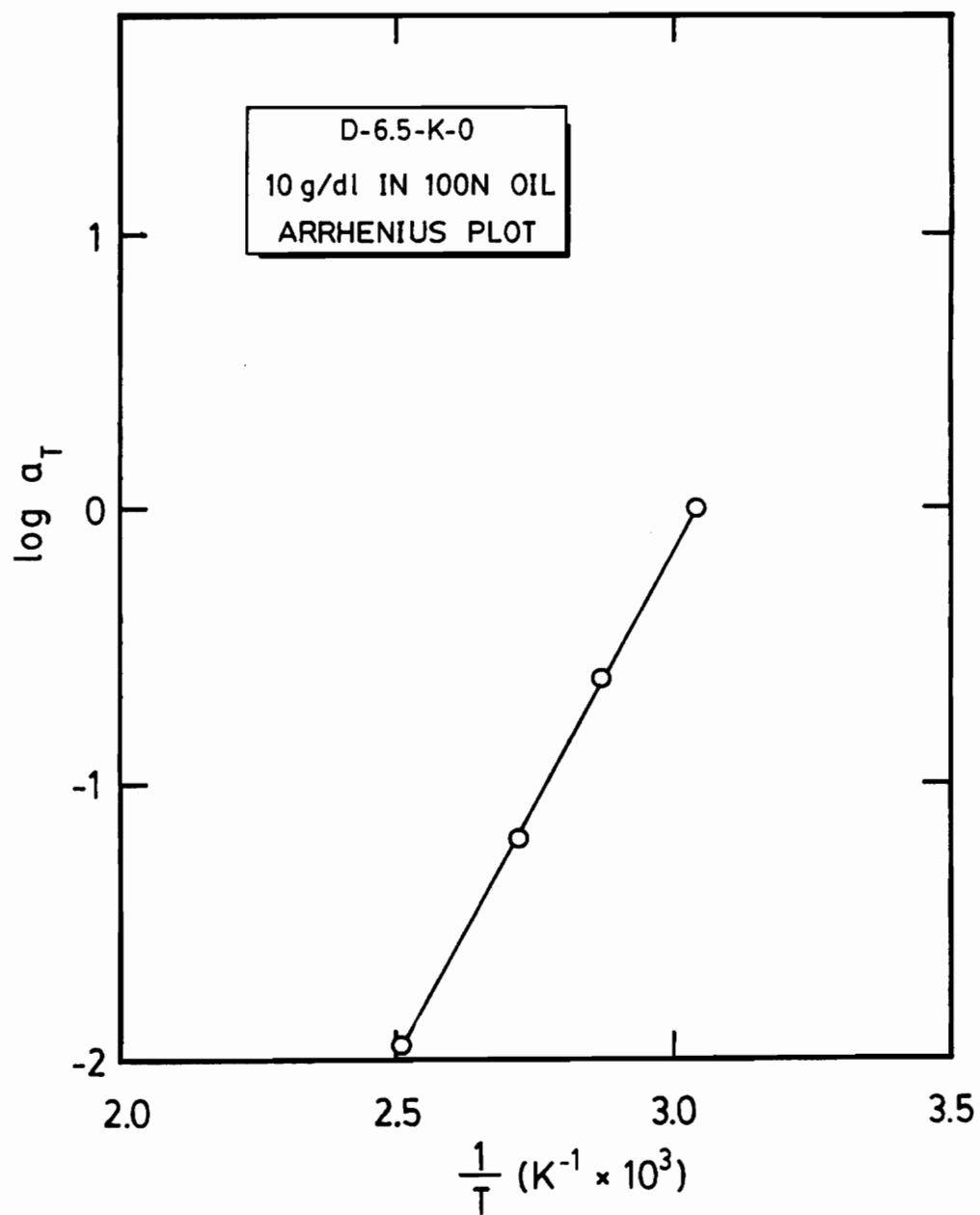


Figure 81. Plot of log shift factor vs. $1/T$ for D-6.5-K-0 in 100N oil (10 g/dl).

low Deborah numbers (< 1) it is viscous. Increasing temperature obviously reduces λ_e , the characteristic response time of the material. Since the transition from viscous to elastic behavior should occur at the same Deborah number for all temperatures, equation (5.19), i.e. $N_{De} = \lambda_e \omega$, indicates that the decreasing λ_e will result in the transition occurring at higher frequencies as observed.

Figures 82, 83, and 84 illustrate the dynamic behavior of T-34-K-0 in 100N oil at a concentration of 5 g/dl and at temperatures of 30, 50, and 70°C, respectively. Composite plots of G' and G'' are shown in Figures 85 and 86. The curves are obviously not superposable. Again, the terminal region is observed to shift to higher frequencies with increasing temperature, while the transition to glass-like behavior seems to remain at essentially the same frequency. It is clear that the terminal slopes of 2 for G' and 1 for G'' are reached only by the 30°C curve and not by the two higher temperature curves. The reason for this change in behavior with temperature is not clear, but it does further illustrate the complexity of these solutions.

Figure 87 shows the steady shear viscosity behavior of D-6.5-ZnAc-100 and D-12-ZnAc-100 at a concentration of 5 g/dl in decalin and at a temperature of 28°C. Both solutions display a viscosity which is independent of shear rate up to a shear rate of about 1. Above this shear rate the solutions are slightly shear thinning. Higher shear rates result in fracture of the solutions and thus any further data would be meaningless. The zero shear viscosity of the D-6.5-ZnAc-100 solution is about 3.9×10^3 poise while that for the D-12-ZnAc-100 solution is about 1.3×10^3 poise. Again, the higher viscosity of the D-6.5-ZnAc-100 solution is due to its higher ionic content and thus higher ionic crosslink density.

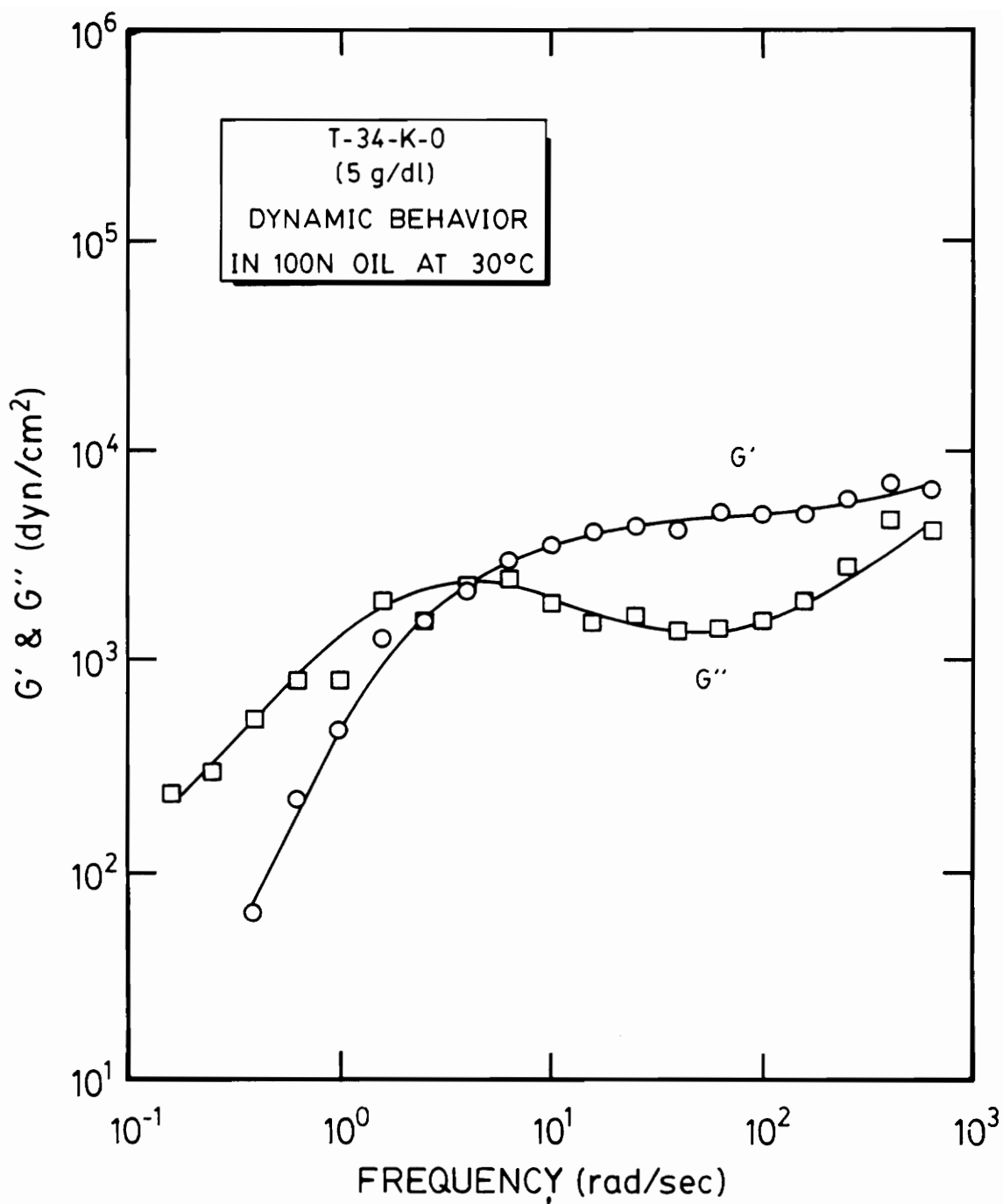


Figure 82. Dynamic behavior of T-34-K-0 in 100N oil (5 g/dl) at 30°C.

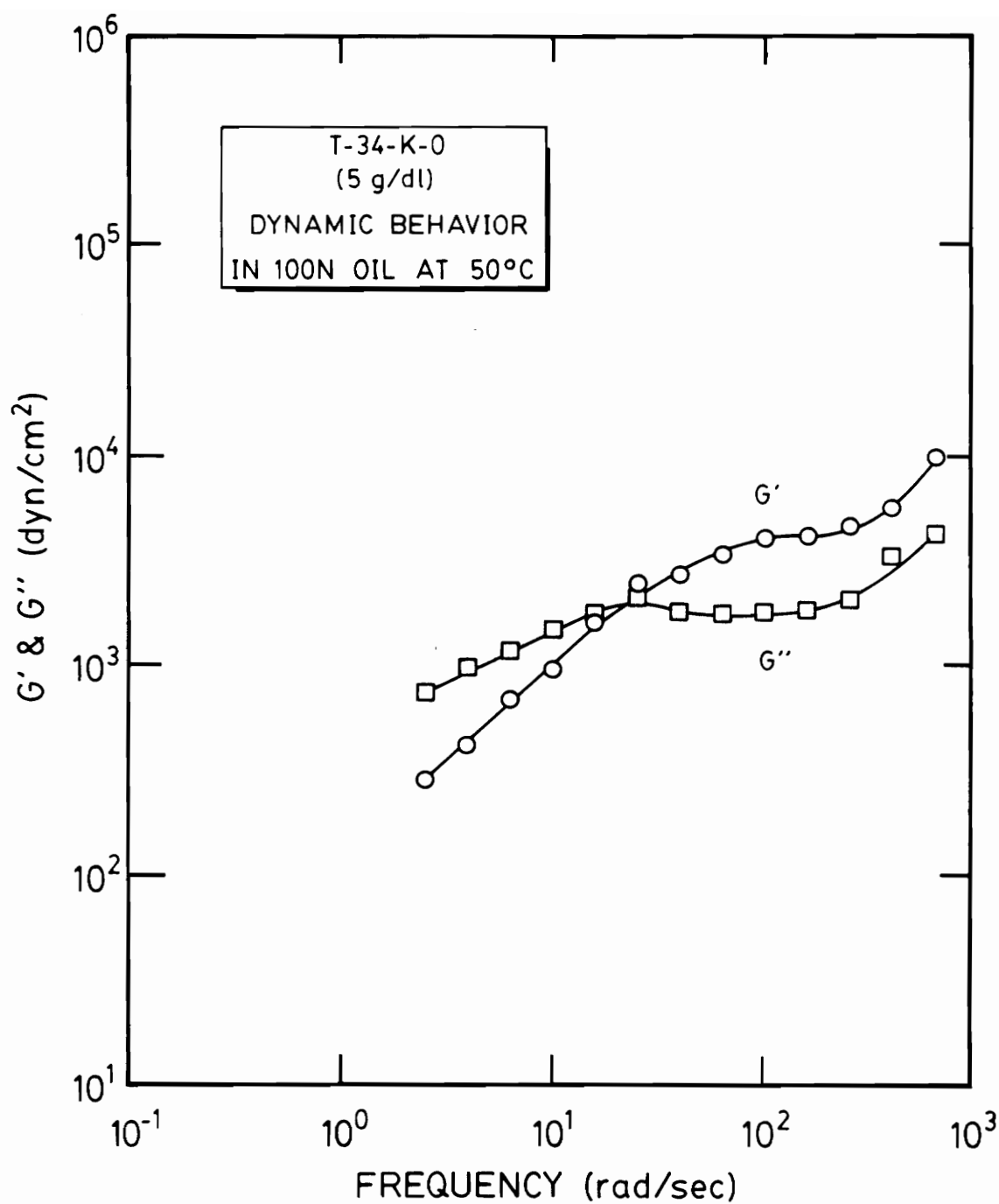


Figure 83. Dynamic behavior of T-34-K-0 in 100N oil (5 g/dl) at 50°C.

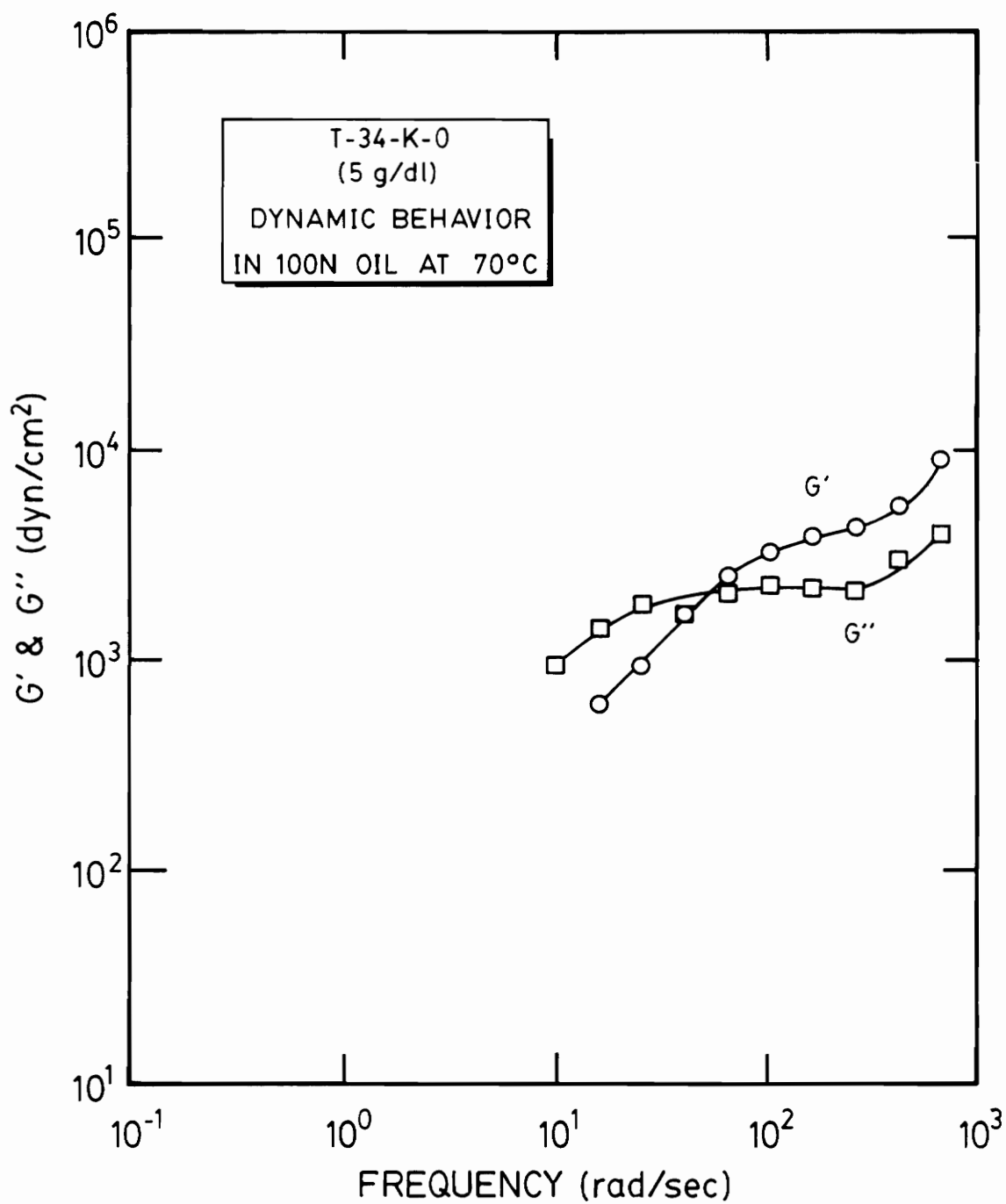


Figure 84. Dynamic behavior of T-34-K-0 in 100N oil (5 g/dl) at 70°C.

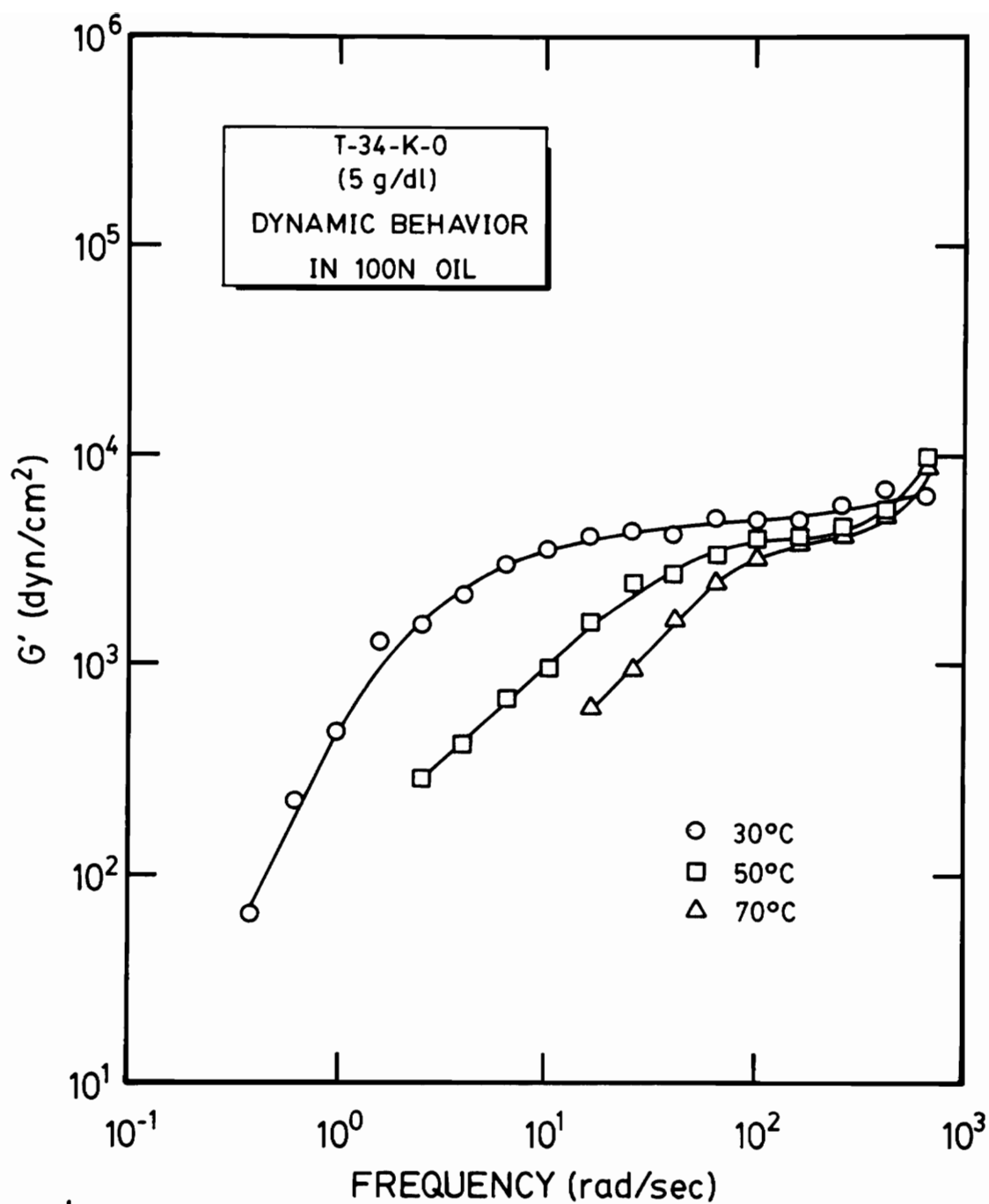


Figure 85. Effect of temperature upon G' of T-34-K-0 in 100N oil (5 g/dl).

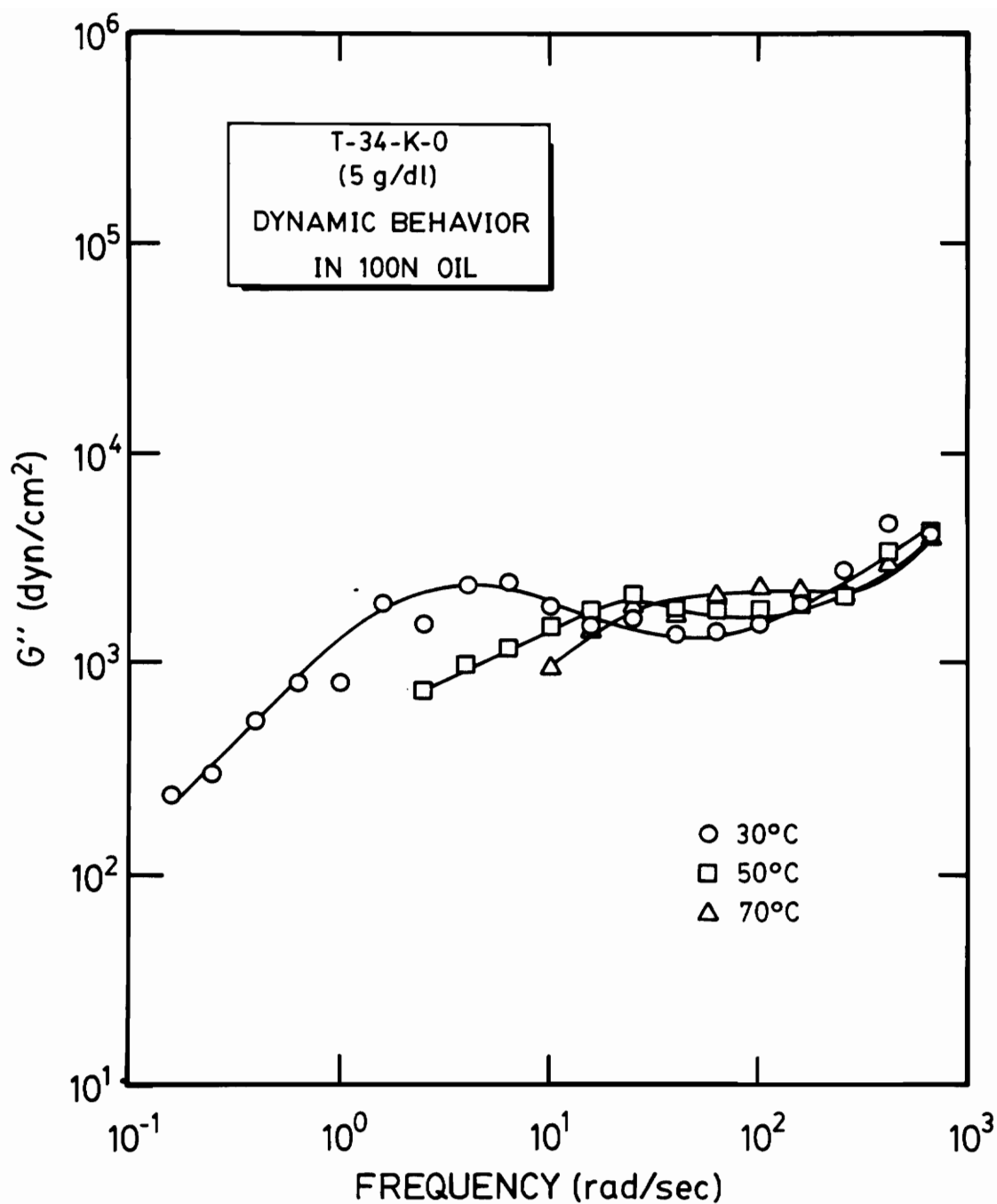


Figure 86. Effect of temperature upon G'' of T-34-K-0 in 100N oil (5 g/dl).

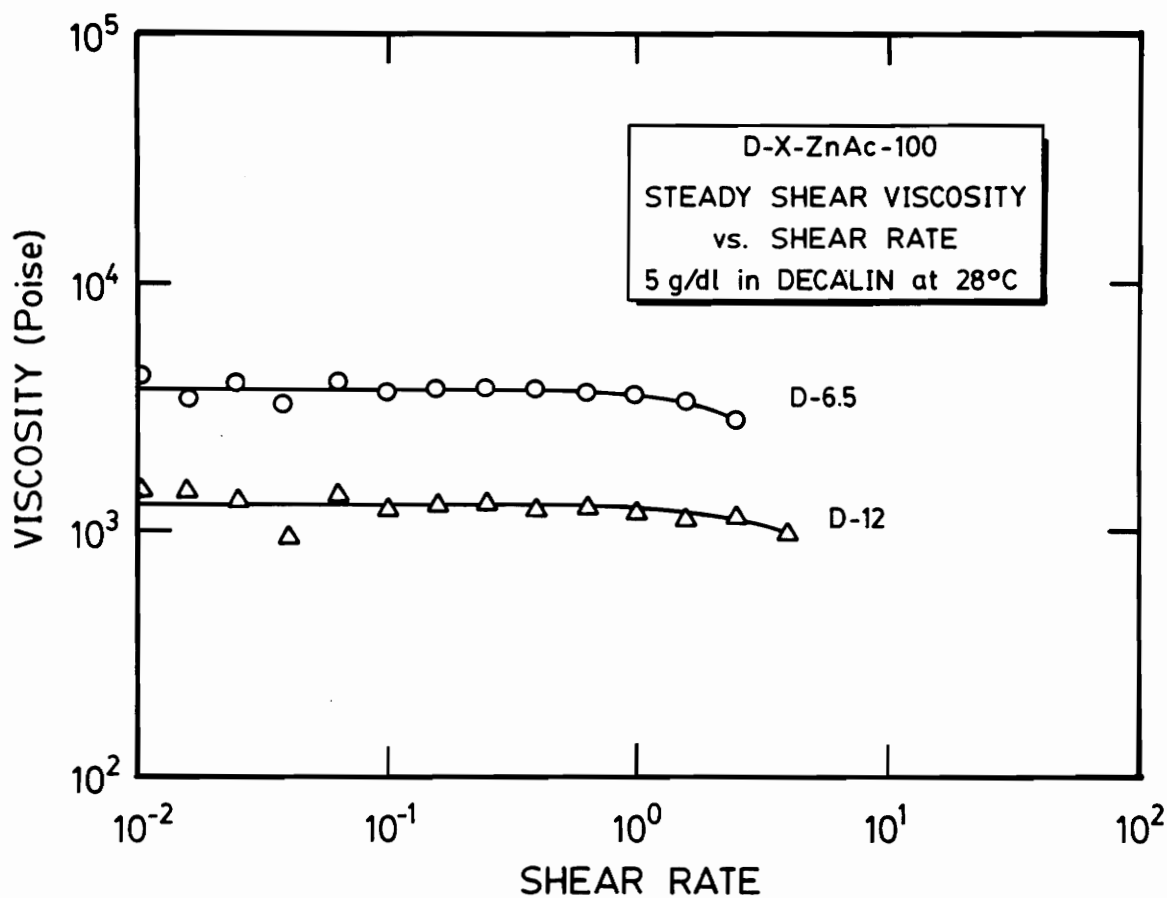


Figure 87. Steady shear viscosity vs. shear rate for D-6.5-ZnAc-100 and D-12-ZnAc-100 in decalin at 5 g/dl and 28°C.

Summary

These studies of the sulfonated polyisobutylene telechelic ionomers in solution have revealed some very interesting features. Gelation occurs in nonpolar solvents at very low concentrations (1-2 g/dl). The gelation concentration is dependent upon such variables as molecular architecture, molecular weight, neutralizing cation, excess neutralizing agent, and solvent polarity. In polar-nonpolar solvent mixtures, the temperature-dependent interaction between the polar solvent molecules and the ionic groups may result in substantial increases in solution viscosity with increasing temperature. The dynamic behavior of sulfonated polyisobutylene telechelic ionomers in nonpolar solvents is highly dependent upon the neutralizing cation. Neutralization with ionic cations such as K^+ and Ca^{2+} can result in solutions which behave as a network over the range of accessible experimental frequencies, while less ionic cations such as Zn^{2+} result in solutions which behave as a network at higher frequencies but flow at lower frequencies. A higher molecular weight nonpolar solvent such as a paraffinic oil interferes with potassium sulfonate and calcium sulfonate interactions enough to cause these solutions to flow at low frequency and exhibit much lower viscosities. The unusual behavior of these solutions suggests that sulfonated polyisobutylene telechelic ionomers might be useful as viscosity control agents in certain applications.

Mechanical and Viscoelastic Behavior of Carboxylated Elastomeric Telechelic Ionomers in Bulk

The carboxylated elastomeric telechelic ionomers provide an interesting comparison with the sulfonated polyisobutylene telechelic ionomers. First, the carboxylate groups

would be expected to interact with one another differently than the sulfonate groups and thus these two types of materials should exhibit different properties. Second, because the polyisoprene backbone used in the carboxylated elastomeric telechelic ionomers is polymerized anionically rather than cationically, the polydispersity is less than 1.2 compared with 1.7 or greater for the sulfonated polyisobutylene telechelic ionomers. Thus the molecular weight and therefore the resulting network structure might be viewed as being better defined for these materials.

Both the solution behavior and the bulk viscoelastic behavior of the carboxylated elastomeric telechelic ionomers have been studied extensively by Broze et al. [46,63,75-80]. However, the behavior of these materials at large deformations was not investigated. The typical mechanical properties, such as stress-strain behavior, ultimate properties, permanent set, hysteresis, etc. give information which is important in utilizing materials in engineering applications, as well as aiding in the determination of whether or not a particular material is suitable for such applications. It was therefore considered to be of importance to study the mechanical properties of these materials.

This section on carboxylated elastomeric telechelic ionomers is divided into several subsections. The first concerns the effect of molecular weight and cation valence upon the mechanical properties of linear carboxy-telechelic polyisoprene. The second considers a linear carboxy-telechelic polyisoprene of $15000 \bar{M}_n$ which was neutralized with a large number of monovalent and divalent cations. The effect of these different cations upon the mechanical behavior is discussed in detail. The third section is concerned with the effect of four different amines (which are able to form complexes with nickel) upon the mechanical properties of the linear carboxy-telechelic polyisoprene of $15000 \bar{M}_n$ neutralized with nickel methoxide. The fourth section deals with the same prepolymer which was neutralized with various amounts of titanium(IV) isopropoxide. The effect of the amount of titanium upon mechanical properties is discussed, and these properties

are compared with those of materials neutralized with other cations. Finally, the fifth section concerns a completely different material - a linear polybutadiene of 4000 \overline{M}_n which is terminated with amine groups complexed with nickel, copper, and iron. Dr. Joo H Song obtained most of the mechanical property data on these materials and his contributions are gratefully acknowledged.

Effect of Molecular Weight and Cation Valence on Mechanical Properties

The effect of molecular weight on the stress-strain behavior of the materials stoichiometrically neutralized with barium is shown in Figure 88. Both the modulus and the stress at constant strain are observed to increase with increasing molecular weight. This behavior is apparently due to the increase in the number of entanglements per chain as molecular weight increases. This would mean that entanglement effects are more important than ionic crosslinking effects in this molecular weight range and for this particular cation. If ionic crosslinking effects were more important, then the stress-strain curves would shift to higher stresses with decreasing molecular weight due to the lower molecular weight between crosslinks. Recall that for the sulfonated polyisobutylene telechelic ionomers, which exhibit very strong ionic associations, this is what is observed. (See Figure 10 on page 39.) The dominance of entanglement effects over ionic crosslinking effects is a somewhat different conclusion than that reached by Jérôme and Broze [80] based on the viscoelastic behavior of magnesium-neutralized materials. These workers observed a transition from behavior dominated by ionic interactions to behavior dominated by entanglements at approximately 20000 \overline{M}_n . The storage modulus G' was observed to increase as \overline{M}_n was increased from 15500 to 20000 to 36000, and then to increase with further increases in molecular weight. This different behavior may be due to the basic difference in type of deformation (steady extension vs. dynamic shear) and

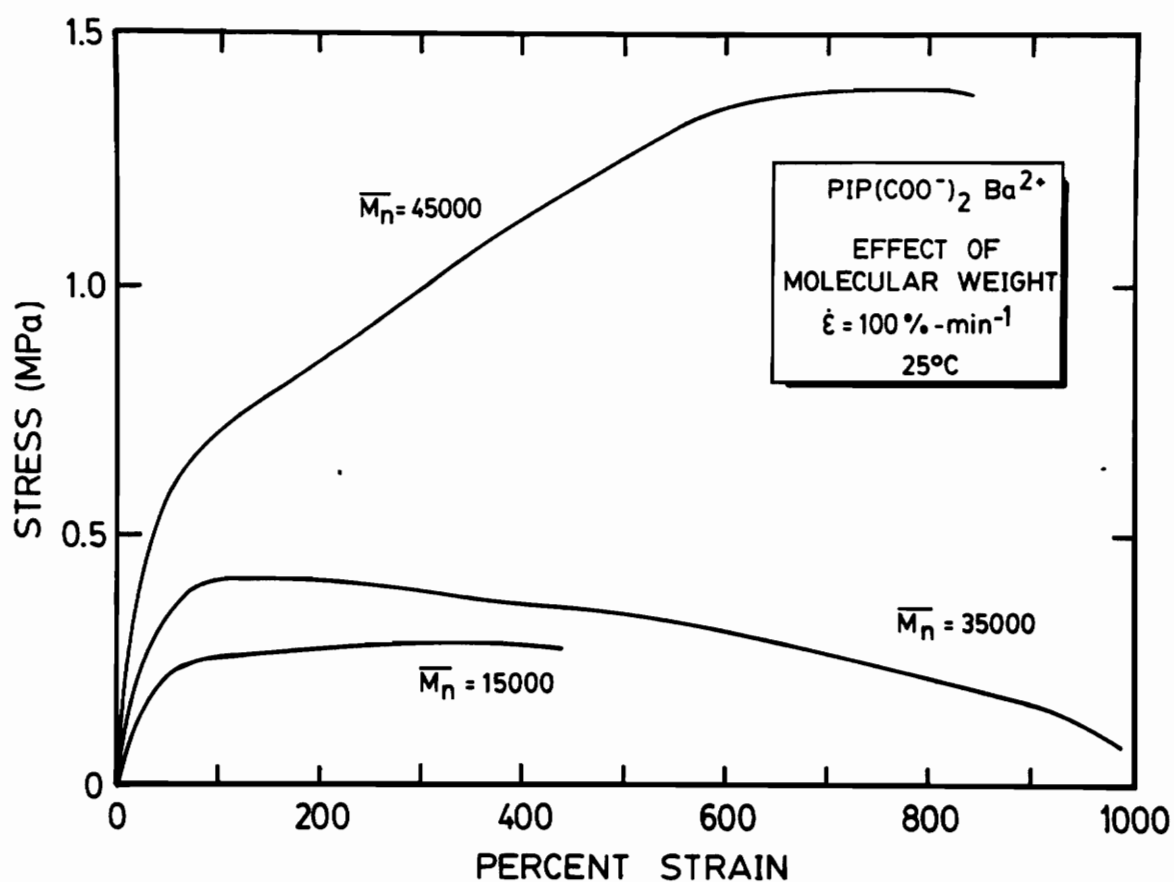


Figure 88. Effect of molecular weight on the stress-strain behavior of barium neutralized materials.

the difference in cations (barium vs. magnesium) may also play a role. It will become clear in the next section that magnesium neutralized carboxy-telechelic polyisoprene displays much stronger ionic bonding than that neutralized with barium. It is possible that the more strongly interacting magnesium neutralized carboxy-telechelic polyisoprene might show a different dependence upon molecular weight.

Figure 89 shows the stress-strain behavior of the zirconium-neutralized materials. In this case the trend is reversed from that observed for the barium materials in that the lower molecular weight material displays a higher modulus and higher stress values. The inorganic crosslinks in this material which, as described in Chapter IV are -Ti-O-Ti- intermolecular bridges, are likely polyfunctional (≥ 3) and the material should thus display a more network-like character than the barium material. (Recall that five times the stoichiometric amount of titanium was added.) A lower molecular weight would lead to a higher crosslink density and thus a higher stress at a given elongation as observed. A similar dependence of stress-strain behavior upon molecular weight has been observed by Bagrodia et al. [84] for sulfonated polyisobutylene telechelic ionomers.

Figure 90 shows the effect of cation valence on the stress-strain behavior at an approximately constant molecular weight of 14500-15000. For the zirconium- and aluminum-neutralized materials, Young's modulus is approximately the same, while it is substantially lower for the barium-neutralized material. The Ba^{2+} and Al^{3+} materials were both stoichiometrically neutralized and interact ionically rather than covalently as the Ti^{4+} . This suggests that the crosslink functionality and/or crosslink density may be similar for the zirconium and aluminum materials but are lower for the barium material. At higher extensions stress decreases in the order $\text{Zr} > \text{Al} > \text{Ba}$. The higher stresses observed for the zirconium material are believed to be due to the fact that the bonds are more permanent and are also of higher functionality because of the cation valence and the neutralization pathway. The differences in the behavior of the carboxy-telechelic

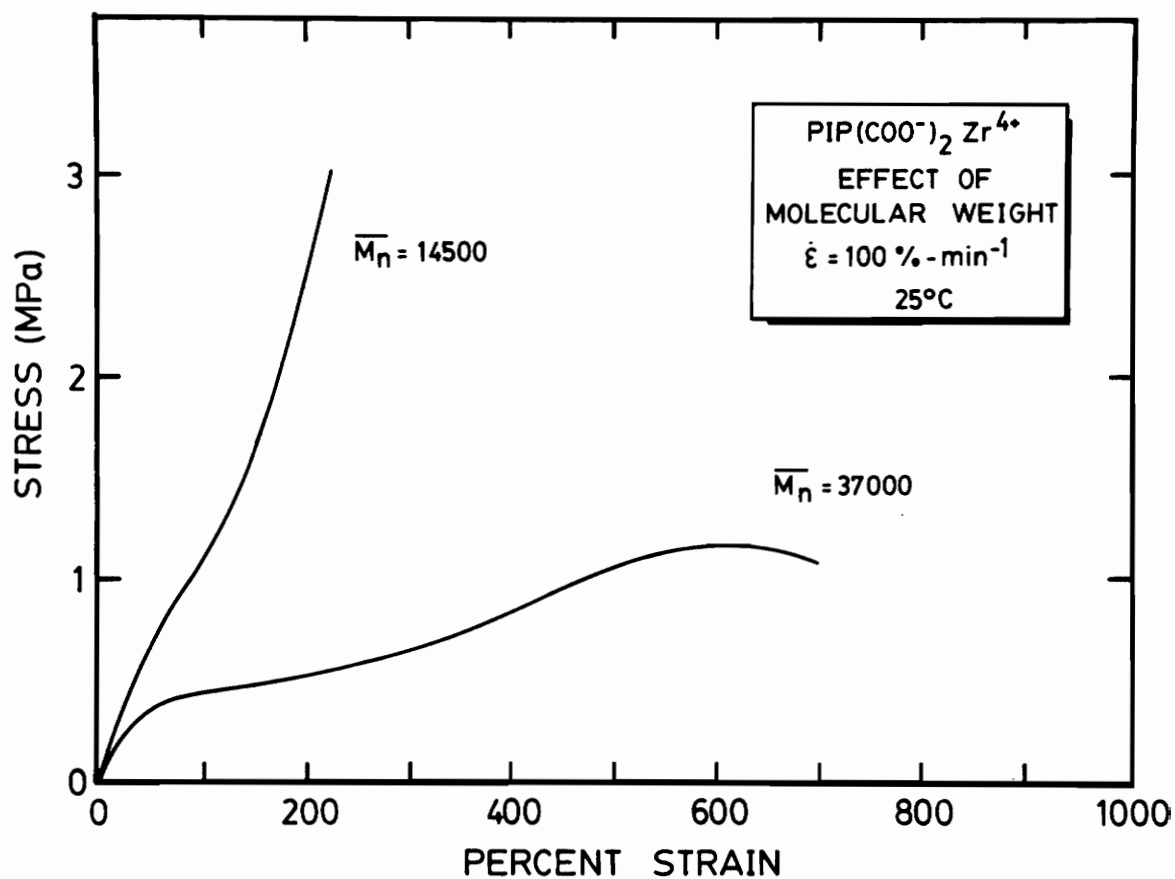


Figure 89. Effect of molecular weight on the stress-strain behavior of zirconium neutralized materials.

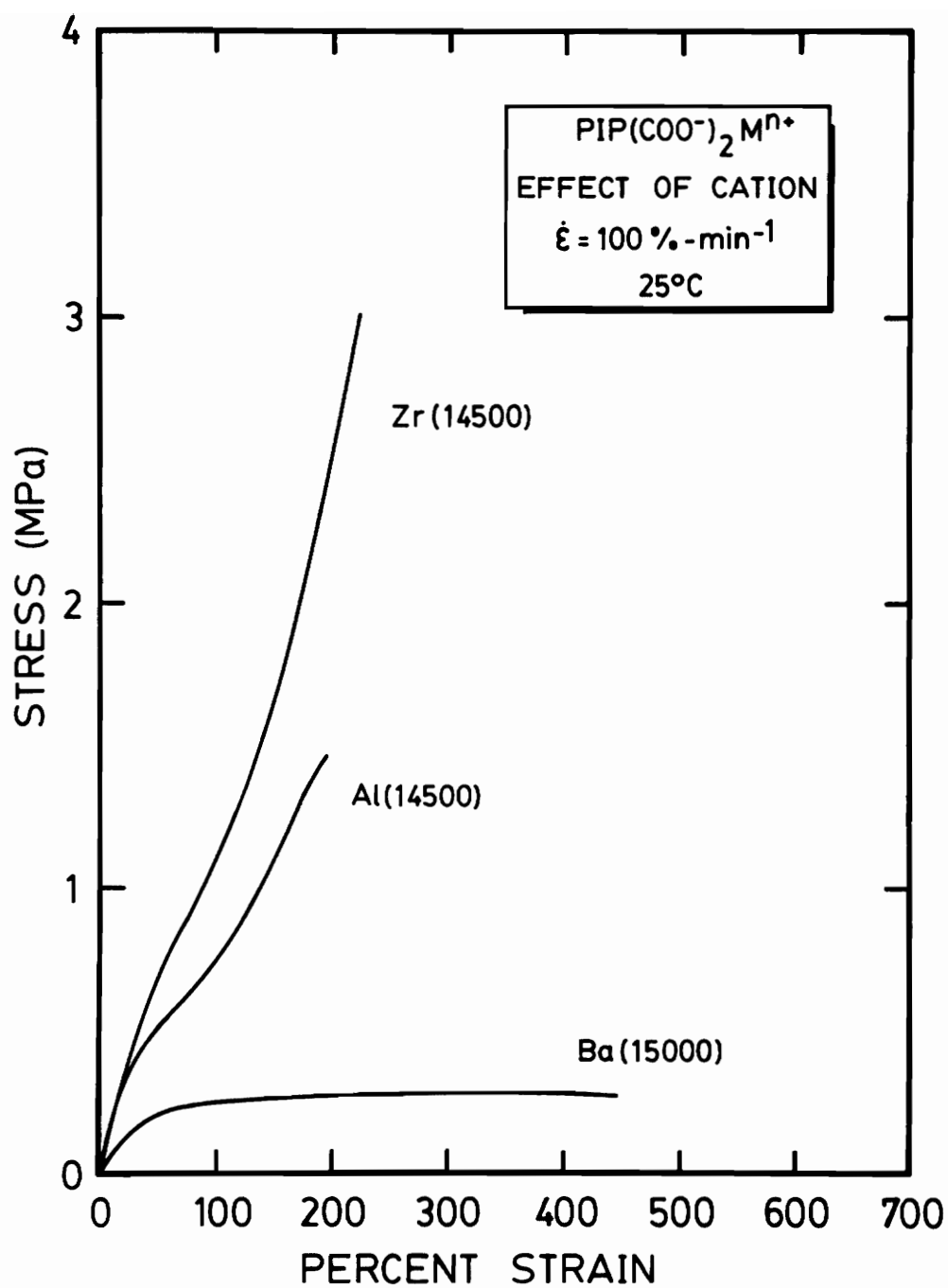


Figure 90. Effect of cation valence on the stress-strain behavior of materials in molecular weight range of 14500-15000.

polyisoprene neutralized with aluminum and barium are apparently due to the differences in cation valence.

Stress relaxation results for the barium and zirconium materials are shown in Figures 91 and 92, respectively. The strains used were 25% for the barium materials and 10% for the zirconium materials, resulting in approximately the same initial stress levels for all of the materials. (The zirconium materials were the only materials which were strained to 10% for stress relaxation.) Although not directly comparable due to the differences in strain, certain conclusions can be drawn. The barium materials display a rather rapid decrease in stress suggesting poor network character. The zirconium materials, particularly the 14500 \overline{M}_n system, maintain stress levels for a longer period of time thus indicating a more permanent network structure. In the case of the barium materials, the relaxation curves for the 15000 and 35000 \overline{M}_n materials are essentially identical. For the 45000 \overline{M}_n barium material, stresses are significantly higher and the rate of relaxation is somewhat slower. For the two zirconium materials, the relaxation curves appear to be quite different. The initial stress for the 14500 \overline{M}_n material is a factor of two higher than that for the 37000 \overline{M}_n material. The 37000 \overline{M}_n material relaxes essentially linearly on this log-log plot while the relaxation curve for the 14500 \overline{M}_n material shows two approximately linear regions intersecting at about 1000 minutes. Relaxation of the 37000 \overline{M}_n material is believed to be due primarily to loss of chain entanglements. Initial relaxation of the 14500 \overline{M}_n material may also be primarily due to disruption of entanglements and chain slippage, finally giving way to breakage of the zirconium network junctions and flow of the material. Similar stress relaxation behavior was, of course, observed for the sulfonated polyisobutylene telechelic ionomers in which there are two linear regions of relaxation with the transition also at about 1000 minutes. However, these were at different strains - 10% for the zirconium neutralized carboxy-telechelic polyisoprenes and 25% for the sulfonated polyisobutylene telechelic ionomers.

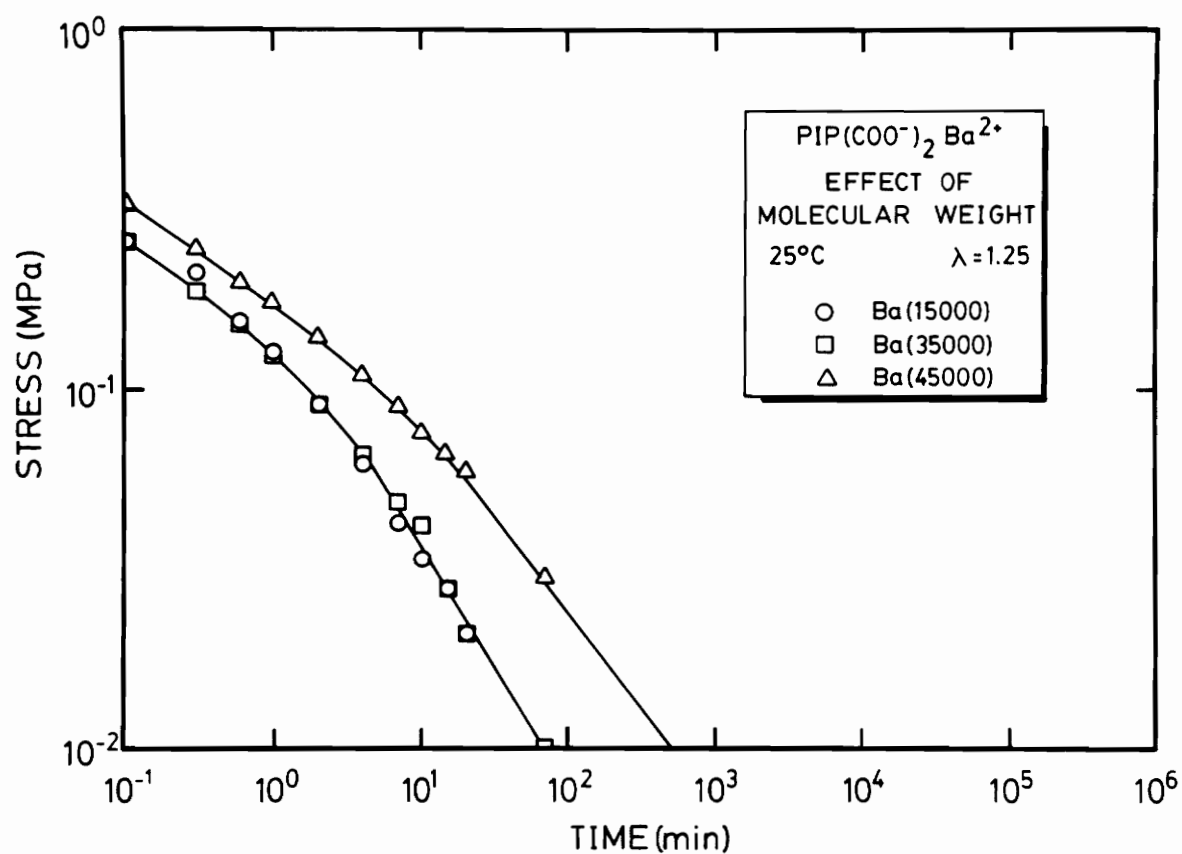


Figure 91. Effect of molecular weight on the stress relaxation behavior of barium neutralized materials.

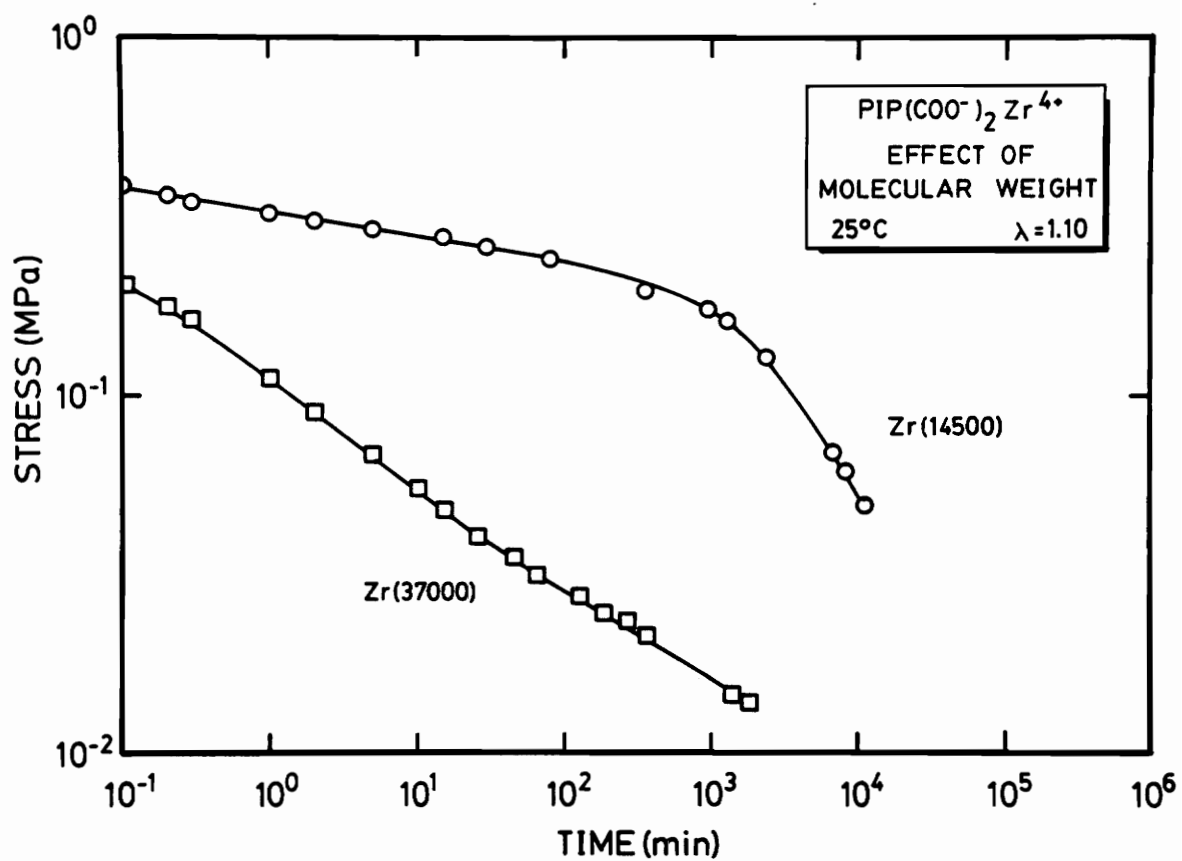


Figure 92. Effect of molecular weight on the stress relaxation behavior of zirconium neutralized materials.

Results of creep experiments on the barium materials are shown in Figure 93. It is clear from the data that the creep rate decreases with increasing molecular weight as would be expected from the stress-strain and stress relaxation behavior. It is interesting to note that the creep rates for the 15000 and 35000 \overline{M}_n materials are quite similar and are greater than that for the 45000 \overline{M}_n material. This agrees with the observation that the 15000 and 35000 \overline{M}_n materials show almost identical stress relaxation behavior and relax faster than the 45000 \overline{M}_n materials. These results again suggest that molecular weight effects are more important than ionic effects in this molecular weight range and for this type of deformation.

Figure 94 shows the instantaneous set as a function of percent strain for the two zirconium materials and the aluminum material of 14500 \overline{M}_n . These data were obtained using the cyclic stress-strain experiment described in Chapter IV. Both of the low molecular weight materials broke in the range of 100-200% strain. The 37000 \overline{M}_n material broke above 550% strain. Comparing this to the percent set data for the trifunctional sulfonated polyisobutylene telechelic ionomers shown in Figure 27 on page 87, it is seen that the 37000 \overline{M}_n zirconium material shows about 10 times the amount of set shown by the sulfonated ionomers at all strains. Thus, even though this material showed the best overall mechanical properties and the most permanent network of the carboxylated elastomeric telechelic ionomers discussed to this point, the stability of the network upon deformation is clearly not as good as the sulfonated polyisobutylene telechelic ionomers. This is likely to be due both to the linear nature of the polyisoprene system as well as the difference in the strength of interactions of carboxylate groups as compared to sulfonate groups. Recall that Lundberg and Makowski [58] demonstrated that sulfonated polystyrene shows much stronger ionic association than carboxylated polystyrene.

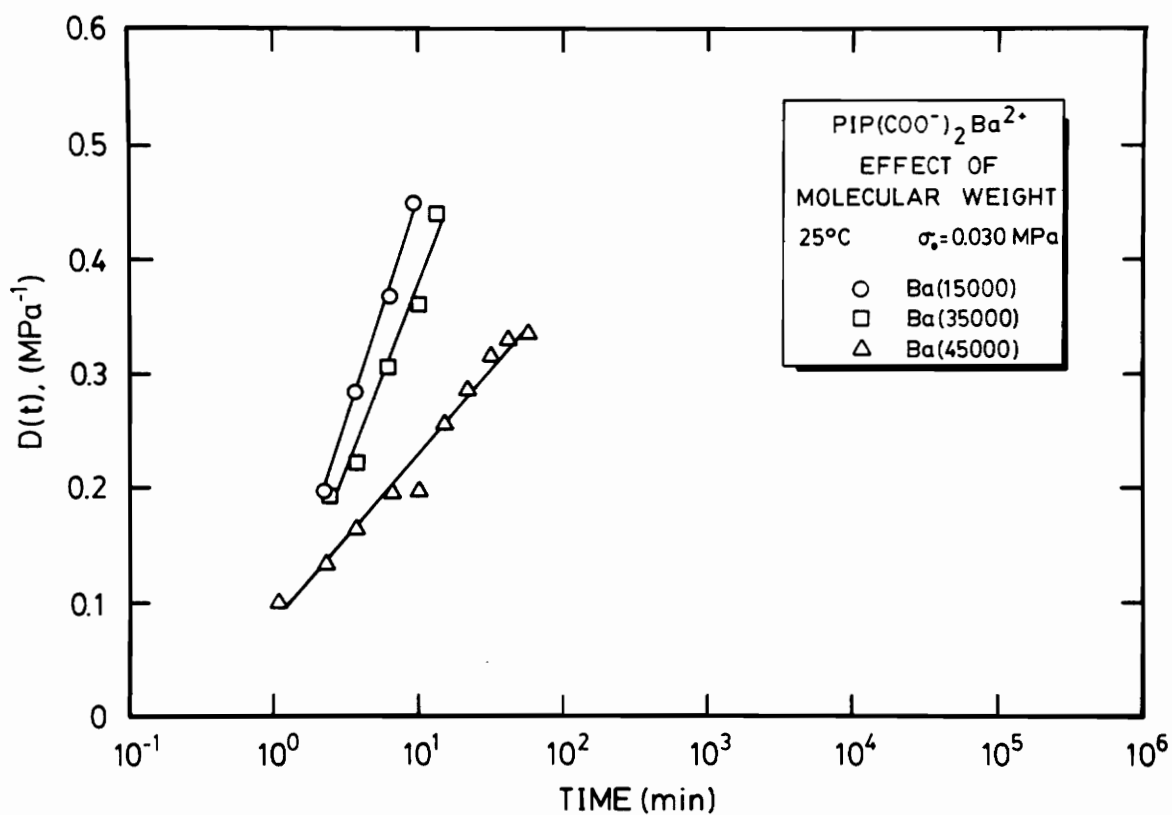


Figure 93. Effect of molecular weight on the creep behavior of barium neutralized materials.

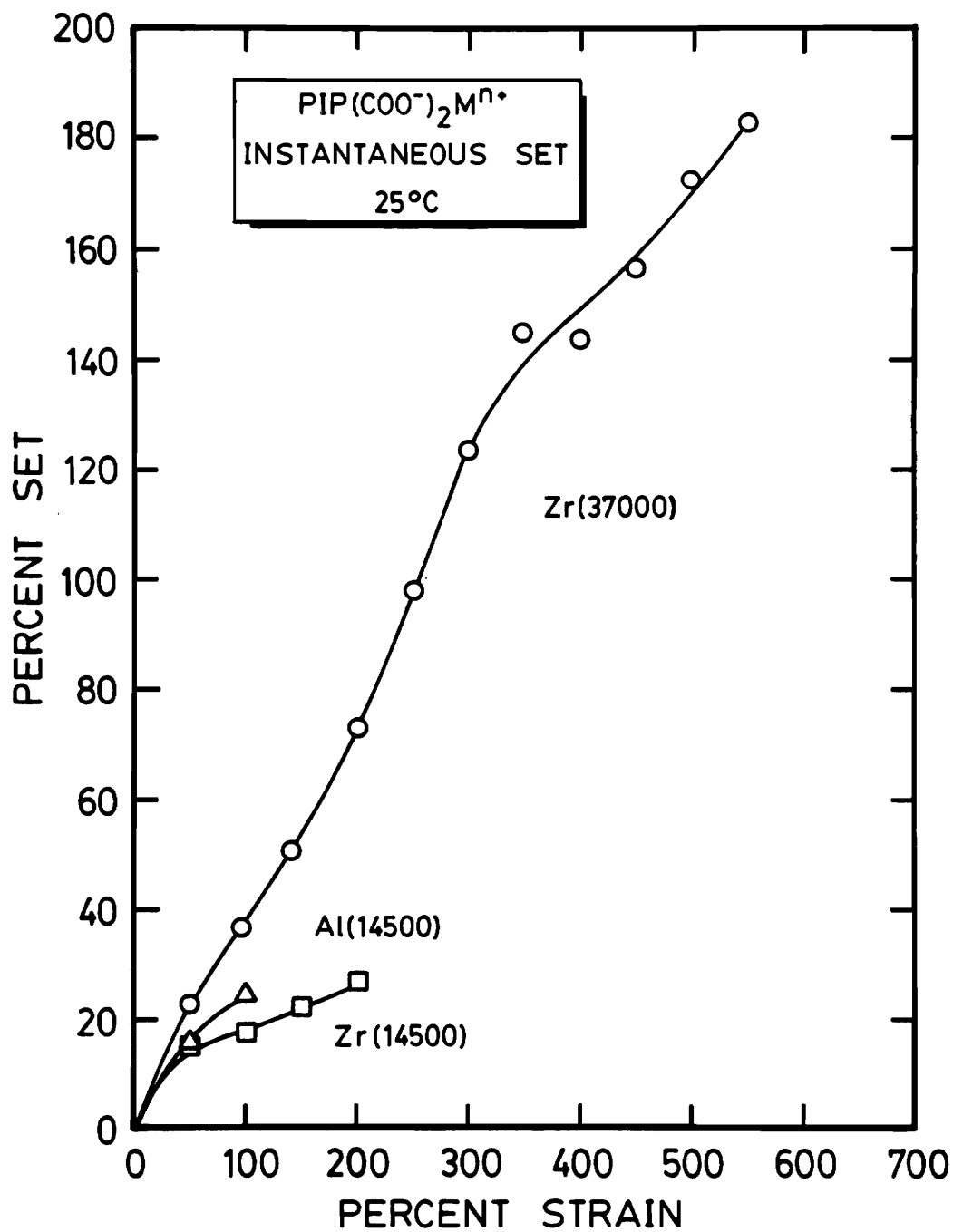


Figure 94. Instantaneous set behavior of the materials neutralized with aluminum and zirconium.

In summary, the molecular weight dependence of stress-strain behavior for carboxylato-telechelic polyisoprene in the range of 15000-45000 \overline{M}_n is dependent upon the neutralizing cation. For barium neutralized materials, modulus and stress increase with increasing \overline{M}_n indicating the dominance of entanglement effects over ionic effects. This conclusion is supported by creep results in which the creep rate is observed to decrease with increasing molecular weight.

For zirconium neutralized materials the reverse trend in stress-strain behavior is observed, i.e. modulus and stress increase with decreasing molecular weight. This suggests the formation of a more well-developed and permanent network induced by the -Zr-O-Zr- intermolecular bridges. Stress relaxation results suggest a similar conclusion. Relaxation of the zirconium neutralized materials proceeds more slowly than that of the barium neutralized materials due to the more permanent network.

Cation valence affects the stress-strain behavior rather strongly. Increasing the cation valence tends to increase the observed stresses for the cations studied.

Effect of Monovalent and Divalent Cation Type on Mechanical Properties

A carboxy-telechelic polyisoprene of 15000 \overline{M}_n was neutralized with seven different monovalent and divalent cations in order to further investigate the effect of cation type upon mechanical properties. The cations chosen were Na^+ and K^+ from Group IA of the periodic table, Mg^{2+} , Ca^{2+} , and Ba^{2+} from Group IIA, and Ni^{2+} and Zn^{2+} from the first series of transition metals.

It is known from electrostatics that the attractive force, F , between an anion of charge e_a and a cation of charge e_c is directly proportional to these charges and varies inversely with both the dielectric constant of the medium, ϵ , and the square of the separation distance, a , i.e.

$$F = \frac{1}{\epsilon} \frac{e_A e_C}{a^2} \quad (5.20)$$

It is thus apparent that the two variables of importance in this case are the charge or valence of the neutralizing cation and its size, assuming a primarily electrostatic or ionic interaction. The force of attraction should then increase with increasing valence and decreasing radius of the cation. However, it is found that this holds only within a particular group of the periodic table, and cannot usually be applied across groups [44].

Figure 95 shows the stress-strain behavior at a strain rate of 100% per minute of the carboxy-telechelic polyisoprene of 15000 \overline{M}_n neutralized stoichiometrically with Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Ni^{2+} , and Zn^{2+} . Materials neutralized with cations from Group IA, i.e. Na^+ and K^+ , behave quite similarly. The primary difference is that the Na^+ material is stiff over the entire range of strain, i.e. the stress-strain curve is relatively linear, while the stress-strain curve for the K^+ material displays more curvature and reaches a slightly higher strain. Since the radius of Na^+ (2.23Å) is smaller than that of K^+ (2.77Å) the reason for the observed trend is clear - the smaller ionic radius results in a higher attractive force and thus a stiffer material. Considering the materials neutralized with cations from Group IIA, i.e. Mg^{2+} , Ca^{2+} , and Ba^{2+} , the same trend is observed. The cation with the smallest radius is Mg^{2+} (1.72Å) and the stress-strain curve of the material neutralized with Mg^{2+} shows that the material is stiff and reaches the highest ultimate stress of any of the materials. Both the Ca^{2+} and Ba^{2+} materials display a yielding behavior. The fact that the Ca^{2+} material reaches higher stresses than the Ba^{2+} is the result of the smaller radius of Ca^{2+} (2.23Å) as compared to Ba^{2+} (2.78Å). The two materials neutralized with cations from the first series of transi-

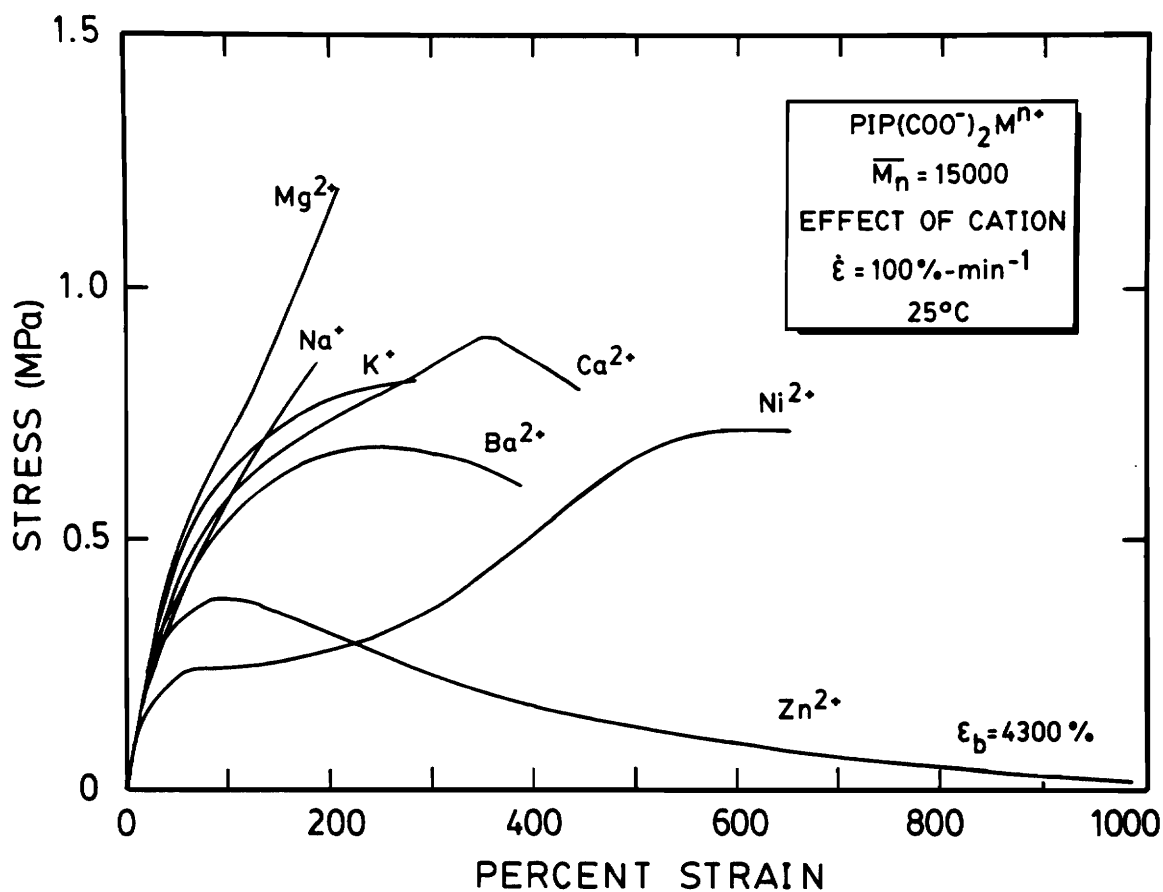


Figure 95. Stress-strain curves for carboxy-telechelic polyisoprene neutralized with various monovalent and divalent cations.

tion metals display quite different behavior due to the less ionic, more coordinative character of their associations. At low strains ($< 40\%$) the Zn^{2+} material behaves similarly to the others. Then it yields and begins to flow with the stress decreasing steadily until failure finally occurs above 4000% strain. The behavior of the Ni^{2+} material is much more interesting. While the stress-strain curve deviates from the others at very low strain, after a short plateau the stress increases again. The stress at break is similar to those of materials neutralized with Group IA and IIA cations (except Mg^{2+}), while the ultimate strain is much higher. Table I compares the ultimate stress and ultimate strain of the materials neutralized with different cations.

The effect of strain rate on the stress-strain behavior sheds further light upon the effectiveness of the various cations in crosslinking the chains. A stronger network resulting from stronger ionic bonding would be expected to result in less strain rate dependence due to less chain slippage. A weaker ionic network would experience more chain slippage and thus more strain rate dependence. Figure 96 shows the effect of strain rate for the materials neutralized with Na^+ and K^+ . Clearly, strain rate has a much larger effect for the K^+ material than for the Na^+ material, again indicating that Na^+ results in stronger crosslinking of the chains due to its smaller size. Figure 97 shows the effect of strain rate on the stress-strain behavior of materials neutralized with Mg^{2+} , the smallest Group IIA cation studied, and Ba^{2+} , the largest Group IIA cation studied. Again, the effect of cation size is clear. The Mg^{2+} material shows very little dependence on strain rate, while the Ba^{2+} material shows a very large dependence. Thus Mg^{2+} , the smallest Group IIA cation, provides stronger ionic bonding. The effect of strain rate upon the two materials neutralized with the transition metals Ni^{2+} and Zn^{2+} is shown in Figure 98. While both show a large dependence on strain rate, they are still quite different. The Zn^{2+} material yields and then flows with constantly reducing stress at the two lowest strain rates, indicating very little resistance to the deformation. For

Table 1. Ultimate Stress and Ultimate Strain of PIP Neutralized with Various Cations

Cation	Ultimate Stress (MPa)	Ultimate Strain (%)
Na ⁺	0.85	170
K ⁺	0.82	280
Mg ²⁺	1.20	210
Ca ²⁺	0.80	450
Ba ²⁺	0.61	385
Ni ²⁺	0.72	660
Zn ²⁺	0	4300

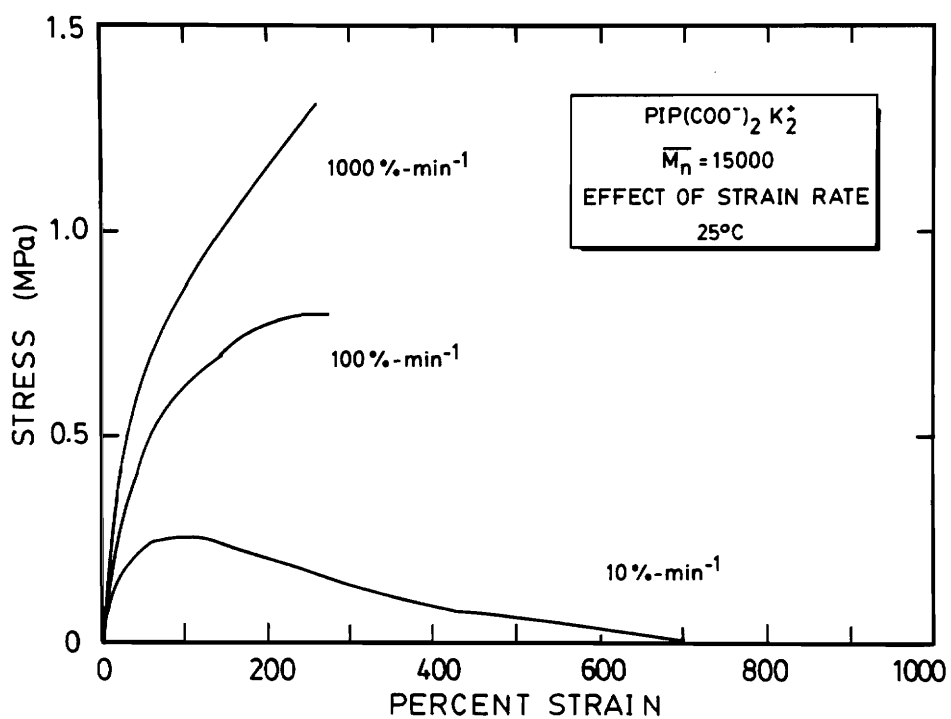
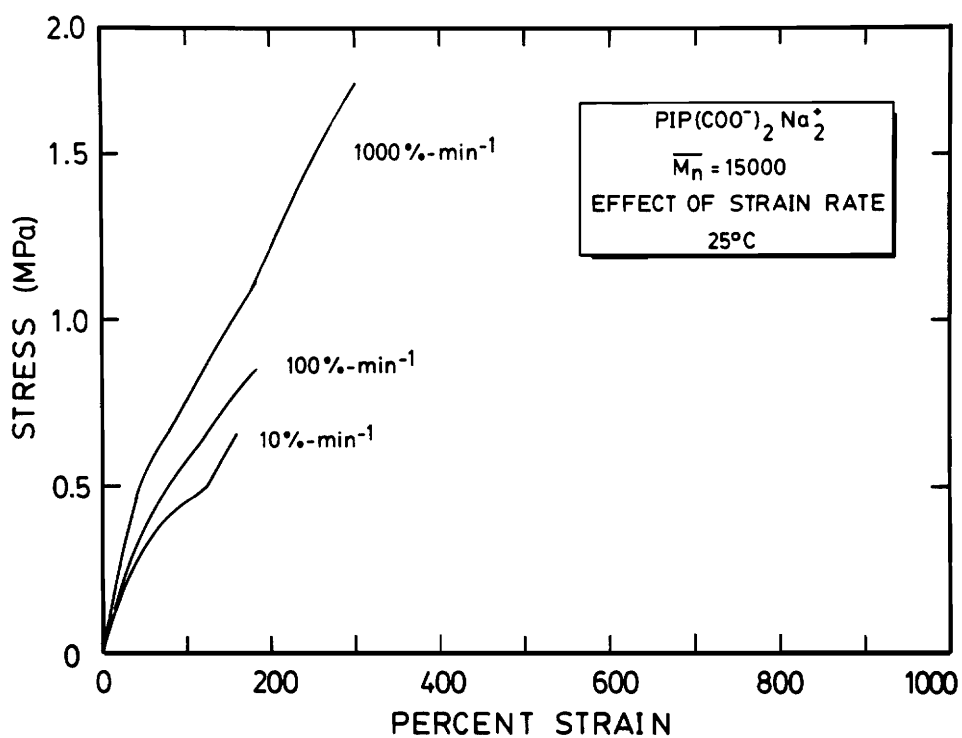


Figure 96. Effect of strain rate on behavior of materials neutralized with Na⁺ and K⁺.

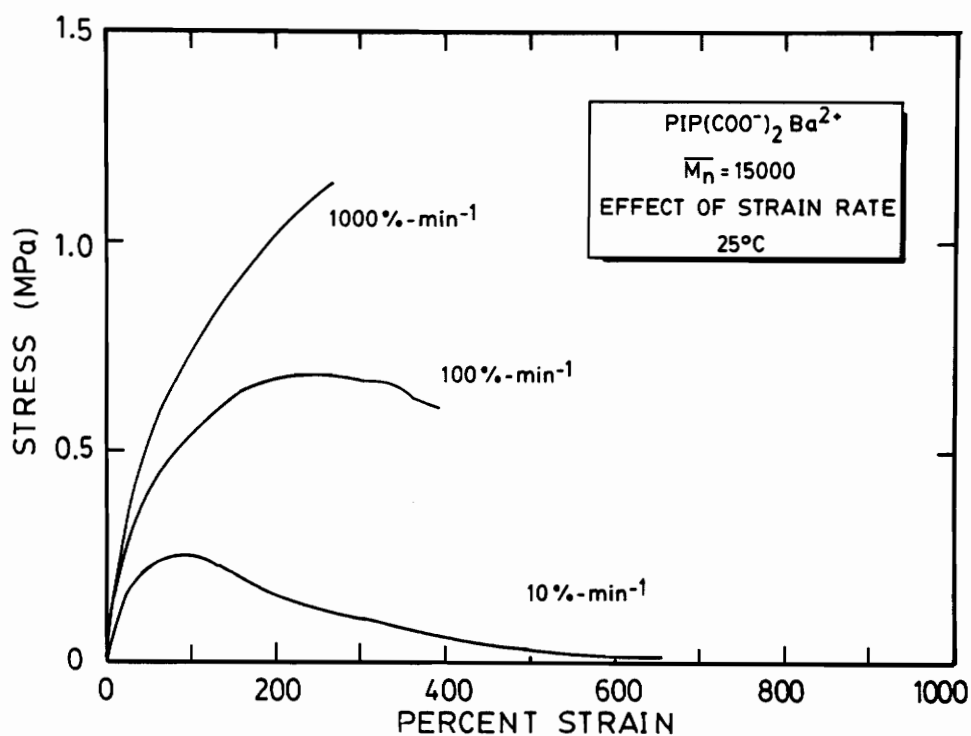
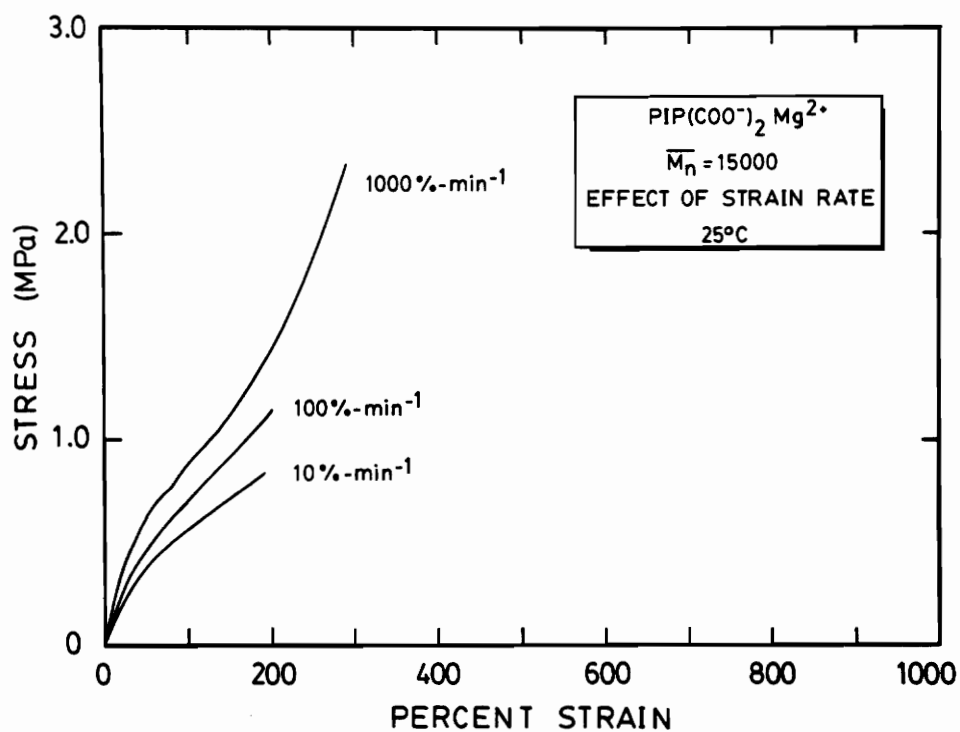


Figure 97. Effect of strain rate on behavior of materials neutralized with Mg²⁺ and Ba²⁺.

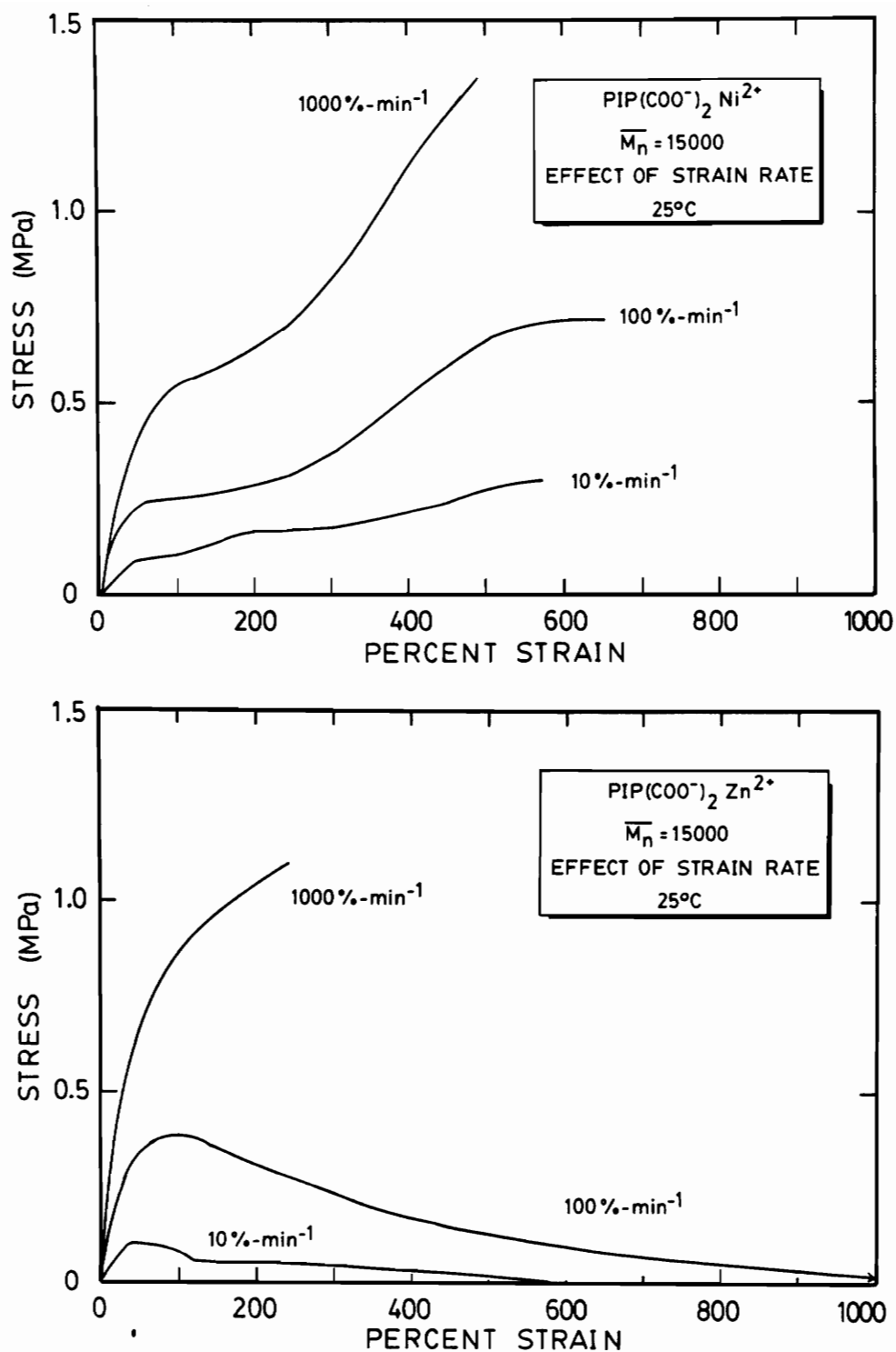


Figure 98. Effect of strain rate on behavior of materials neutralized with Ni^{2+} and Zn^{2+} .

the Ni^{2+} material, stress increases at all strain rates until fracture occurs, indicating that the ionic crosslinks remain quite effective even at high extensions.

Figure 99 shows the stress relaxation and creep behavior for this series of materials. Again, as in the stress-strain experiments, the smallest cations studied in Groups IA and IIA provided the most resistance to flow as might be expected if other factors are assumed not to change. Network stability was greatest for the Mg^{2+} material. Again, for Group IA and IIA materials, network stability decreases with increasing cation size in each group. The Zn^{2+} material relaxes more quickly than any of the others, again due to its less ionic character. It is noted that the shapes of the stress relaxation curves are all very similar except that for the Ni^{2+} material. The rate of relaxation is high for this material at short times, but becomes much slower than for the other materials at longer times. The stress relaxation curve for the Ni^{2+} material actually crosses the curves for all of the materials except Na^{+} and Mg^{2+} during the time window studied. This supports the results of the stress-strain data which show that the Ni^{2+} material behaves very differently from any of the others.

Figure 100 shows the results of thermomechanical experiments on these materials. Figure 100a shows the penetration curves while Figure 100b shows the first derivatives. The flow regions of the two smallest cations, Na^{+} and Mg^{2+} , occur at the highest temperatures with the Mg^{2+} network persisting to the highest temperatures. The flow temperatures decrease with increasing cation size within Group IA and Group IIA. The Zn^{2+} material flows at the lowest temperature. The penetration curve for the Ni^{2+} material is somewhat different than the others in that it is relatively linear, showing only a hint of a rubbery plateau.

The instantaneous set and hysteresis behaviors of these materials are shown in Figure 101. Again, the Na^{+} and Mg^{2+} materials show the tightest network, i.e. low instantaneous set and hysteresis, although they fracture at very low strains. Within Group

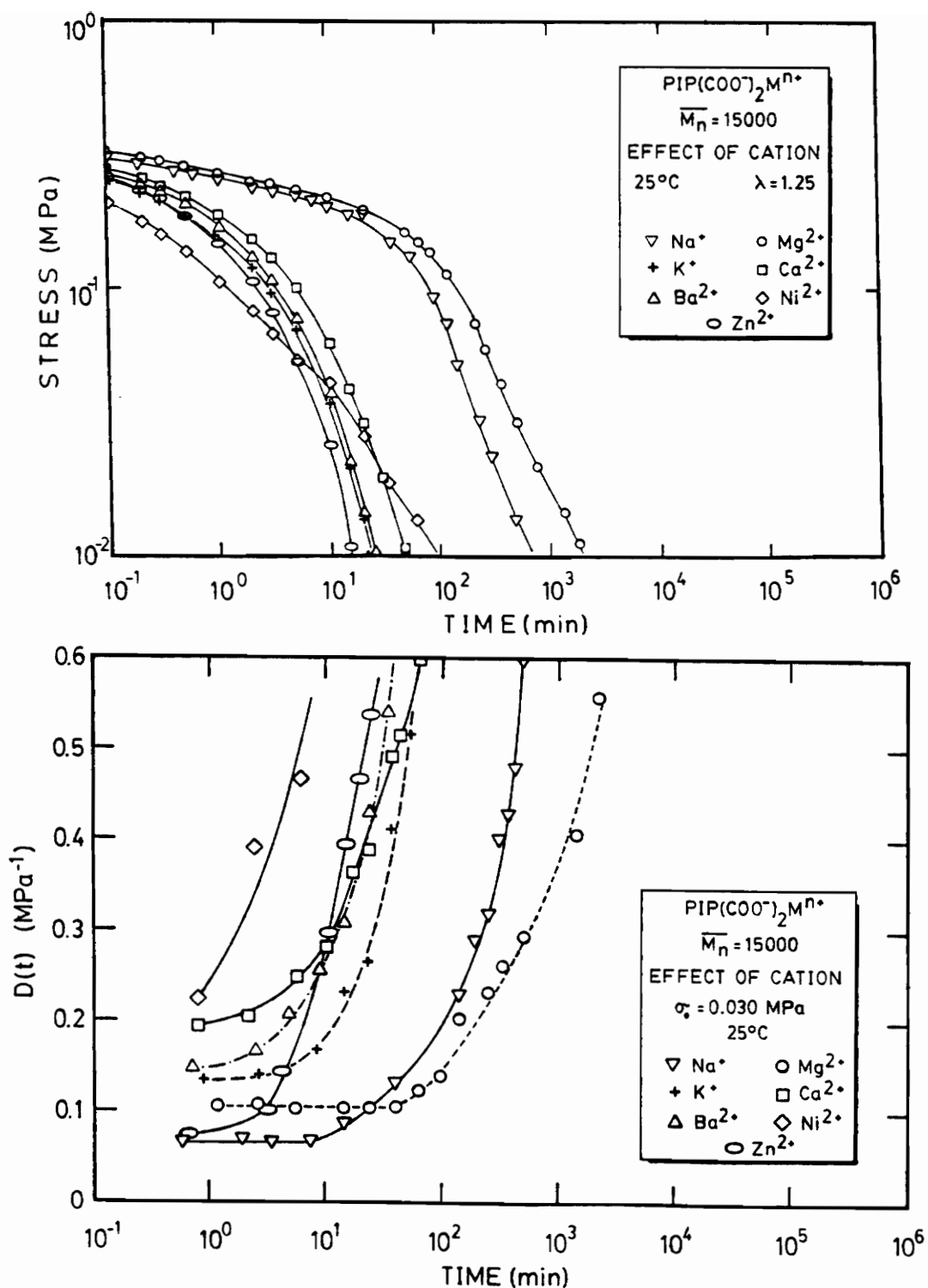


Figure 99. Stress relaxation and creep curves of carboxy-telechelic polyisoprene neutralized with various cations.

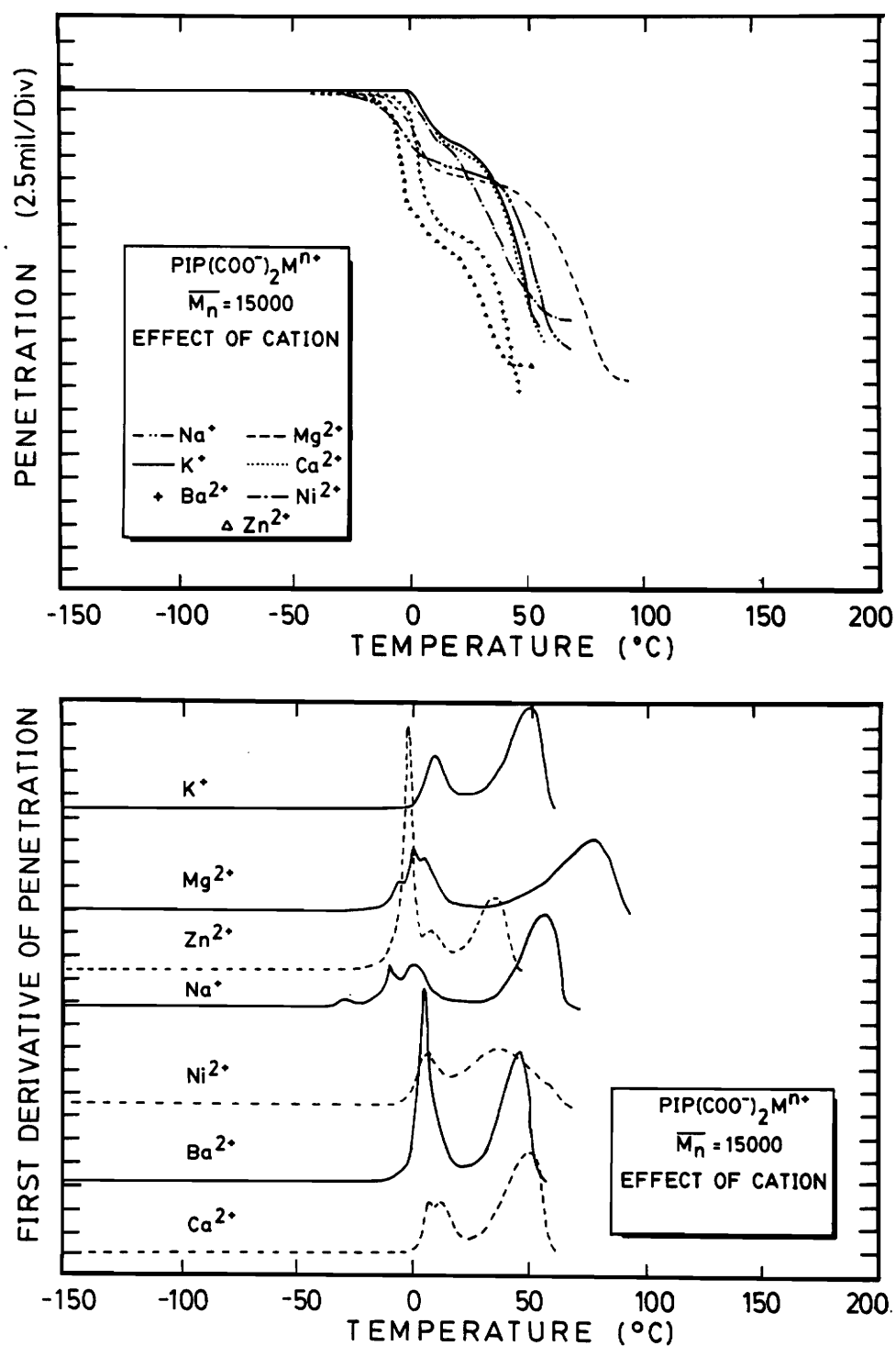


Figure 100. Thermomechanical behavior of carboxy-telechelic polyisoprene neutralized with various cations.

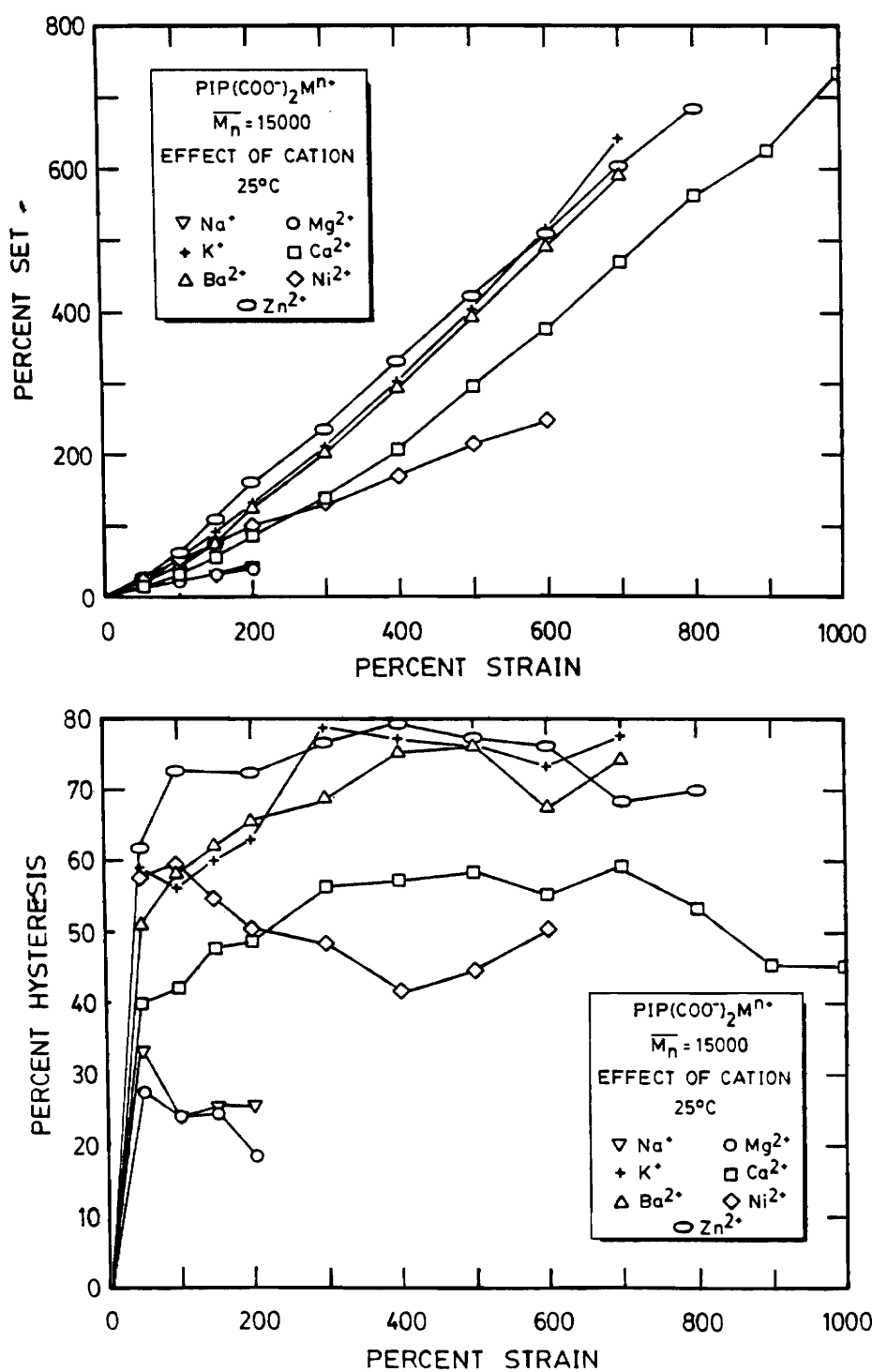


Figure 101. Instantaneous set and hysteresis of carboxy-telechelic polyisoprene neutralized with various cations.

IA and Group IIA both instantaneous set and hysteresis increase with increasing cation size, again indicating that smaller cations result in stronger, more stable networks. Both the instantaneous set and hysteresis of the Ni^{2+} material are much lower than those for the Zn^{2+} material. This supports the other results which indicate that, of these two transition metals, Ni^{2+} is much more effective at crosslinking the carboxy-telechelic polyisoprene than Zn^{2+} .

To further check the network stability of these materials, a sample of each was stretched to 100% strain and maintained at that strain for one week. The samples were then released and recovery was monitored. The Mg^{2+} material fractured during the period of 100% strain. The K^{+} material was found to recover only slightly, recovering to 91% permanent set (or 9% of the 100% strain was recovered) after 10^4 minutes. None of the other materials recovered at all. These results indicate that, compared to the sulfonated polyisobutylene telechelic ionomers, the integrity of the ionic networks formed by these materials is very poor.

Effect of Amines on Mechanical Properties of Nickel Neutralized Materials

Since the material neutralized with Ni^{2+} showed perhaps the most promise as a neutralizing cation to form an elastomer, an attempt was made to reinforce the ionic associations by adding a diamine and a triamine. The diamine was 1,4-diazobicyclic 2.2.2 octane ($\text{C}_6\text{H}_{12}\text{N}_2$) and the triamine was tris(dimethylaminomethyl)phenol ($\text{C}_{15}\text{H}_{27}\text{N}_3\text{O}$). Four different materials were prepared, all being neutralized stoichiometrically with NiCl_2 . In the first, one-half mole of the diamine was added per mole of Ni^{2+} . In the second, one mole of this same amine was added per mole of Ni^{2+} . The third was the same as the second except that one-half mole of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was added

per polyisoprene chain. In the fourth, one-third mole of $C_{15}H_{27}N_3O$ was added per mole of Ni^{2+} .

The stress-strain curves of this series of materials are shown in Figure 102. These curves should be compared with the curve for the material neutralized with nickel methoxide but without amine shown in Figure 95 on page 194. None of the curves shown in Figure 102 reach the stresses displayed by the Ni^{2+} material without amine. The curve for the material with one-half mole of $C_6H_{12}N_2$ per mole of Ni^{2+} turns downward instead of upward, suggesting that the ionic associations may be plasticized instead of reinforced by the amine. The curve for the material with twice as much $C_6H_{12}N_2$ reaches only half the stress of the previous material and then flows, supporting the suggestion that the ionic regions are plasticized. This same material with additional $NiCl_2 \cdot 6H_2O$ reaches higher stresses and does not turn downward, but still does not reach the stresses displayed by the material not modified with amine. Apparently, while the amine plasticizes the ionic associations, the excess Ni^{2+} counteracts this by reinforcing the ionic associations. Of course, the fact that excess neutralizing cation reinforces the ionic associations in sulfonated polyisobutylene telechelic ionomers has already been discussed. Finally, the material with the triamine $C_{15}H_{27}N_3O$ displays quite low stresses and flows to very high extension. Again, apparently the triamine is also plasticizing the ionic regions. Therefore, the attempt to reinforce the ionic associations with amines was unsuccessful, but it did become apparent that excess Ni^{2+} may serve such a purpose.

Mechanical Properties of Materials Neutralized with Titanium

The neutralization of carboxy-telechelic polymers with Group IVA cations has already been discussed to some extent. The metal alkoxide is added in sufficient quantities to cap as many chain ends as possible with carboxylato alkoxy metal groups. The

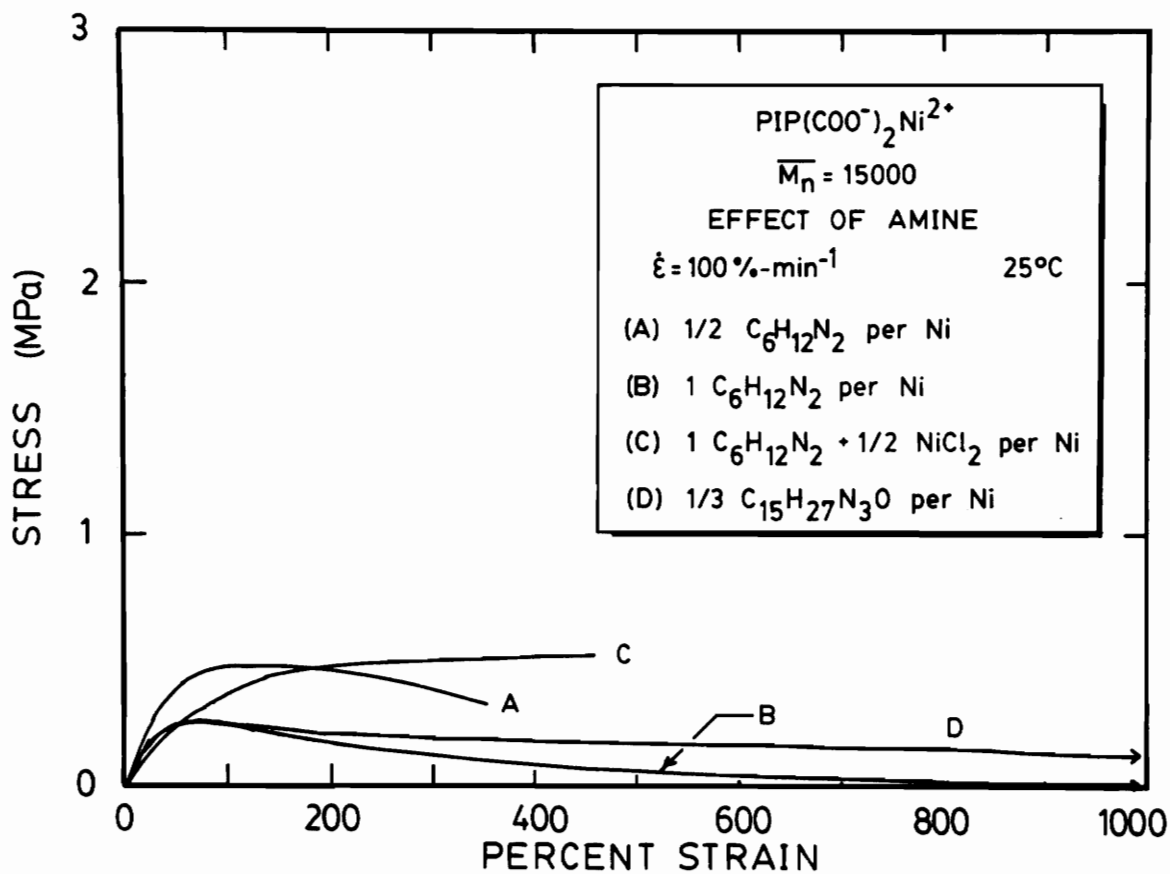


Figure 102. Effect of amines on stress-strain behavior of nickel neutralized carboxy-telechelic polyisoprene.

nonsubstituted alkoxy groups are then hydrolyzed to form metal-oxygen-metal intermolecular bridges. The partial hydrolysis of the excess metal alkoxide gives rise to metal-OH groups which react with the unhydrolyzed metal-O-n.Bu to form the metal-O-metal grouping and n-BuOH as a by-product. Broze et al [78,79] have previously addressed the preparation of these materials as well as their viscoelastic behavior in both bulk and solution.

A series of 15000 \overline{M}_n carboxy-telechelic polyisoprenes was provided by Professor Robert Jérôme which had been reacted with various amounts of titanium (IV) isopropoxide. This series of materials had titanium to polymer ratios (Ti/PIP) of 1/2, 1, 2, and 3. The molar ratio of 1/2 corresponds to stoichiometric neutralization of the classical type, i.e. assuming each tetravalent titanium cation associates with four carboxy endgroups.

Figure 103 shows the stress-strain behavior of this series of materials at a strain rate of 100% per minute, the same strain rate used for earlier comparisons. Clearly, the amount of excess titanium has a very strong effect upon the stress-strain behavior. The material with the Ti^{4+} to polymer molar ratio of 1/2 sustains only a very low stress and flows to an extension of more than 900%. Doubling the Ti^{4+} amount to a molar ratio (Ti/PIP) of 1 more than doubles the maximum stress developed but also reduces the maximum extension to about 400%. Doubling the amount of Ti^{4+} again (Ti/PIP = 2) more than doubles the maximum stress again and reduces the ultimate strain to less than 300%. Increasing the Ti/PIP ratio to 3 further increases the ultimate stress but reduces the ultimate strain only slightly. It is clear that the modulus increases dramatically upon increasing the Ti/PIP ratio from 1 to 2. This is an indication of an increase in the crosslink density or crosslink functionality. Table II gives the ultimate stress, ultimate strain, and modulus as a function of the Ti/PIP ratio.

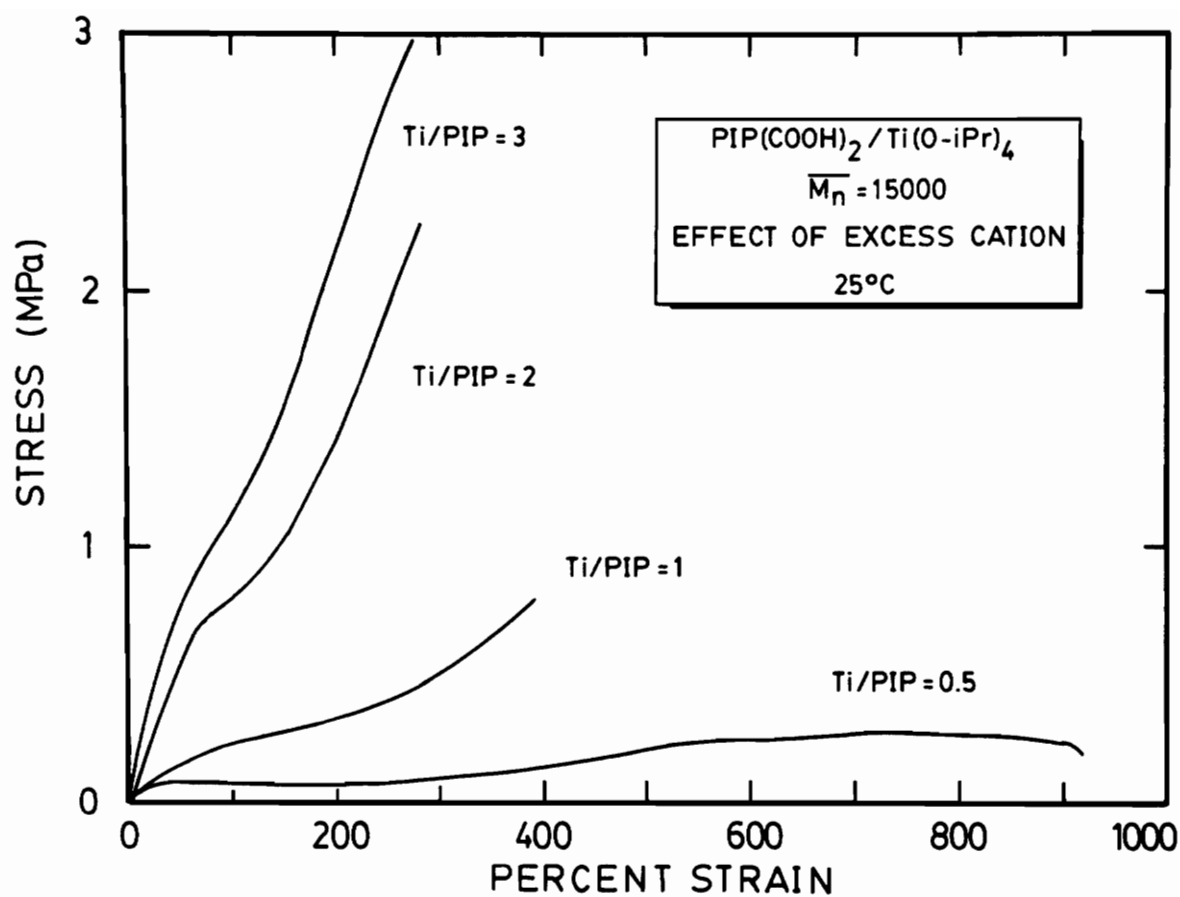


Figure 103. Stress-strain behavior of carboxy-telechelic polyisoprene neutralized with various amounts of titanium (IV).

Table 2. Ultimate Stress, Ultimate Strain, and Modulus of PIP Neutralized with Various Amounts of Titanium

Ti/PIP	Ultimate Stress (MPa)	Ultimate Strain (%)	Modulus (MPa)
1/2	0.19	920	0.31
1	0.80	390	0.31
2	2.27	280	1.10
3	2.97	280	2.30

The effect of strain rate gives further evidence that the network improves as the Ti/PIP ratio increases. Figure 104 shows the effect of strain rate for the materials with Ti/PIP ratios of 1/2 and 1, and Figure 105 gives this data for the materials having Ti/PIP ratios of 2 and 3. Clearly, as the ratio increases from 1/2 to 1 to 2, the strain rate dependence reduces markedly, particularly between 1 and 2. This result suggests that it is in the Ti/PIP ratio range of 1 to 2 that network formation occurs. Increasing the ratio from 2 to 3 has essentially no effect on the strain rate dependence. This supports the modulus data, which shows the largest change when Ti/PIP is increased from 1 to 2.

Figure 106 shows the stress relaxation and creep behavior of these materials. Clearly, both the strength and stability of the network improve as Ti/PIP is increased. The material with a ratio of 1/2 creeps so quickly that it cannot be measured. Increasing the Ti/PIP ratio to 1 markedly stabilizes the material, but it is not until the ratio reaches 2 that a reasonably stable network is formed. Increasing the ratio has little effect upon the stress relaxation behavior except at long times. This, as well as the creep data, suggest that the network is further stabilized by increasing Ti/PIP from 2 to 3.

The thermomechanical behavior of these materials is illustrated in Figure 107. The material with a Ti/PIP ratio of 1/2 displays no evidence of a rubbery plateau. Increasing the ratio to 1 results in a very slight plateau, while both of the materials with a higher ratio exhibit significant and very similar plateaus. This is further indication that network formation really occurs between the ratios of 1 and 2. The dynamic mechanical data shown in Figure 108 suggest similar conclusions. Although the material with a Ti/PIP ratio of 1 shows a reasonable plateau, the plateau modulus is significantly higher for the materials with ratios of 2 and 3.

Figure 109 shows the instantaneous set and hysteresis behavior of these materials. Both set and hysteresis decrease greatly with increasing Ti/PIP ratio. For the materials with ratios of 2 and 3, the instantaneous sets are very similar.

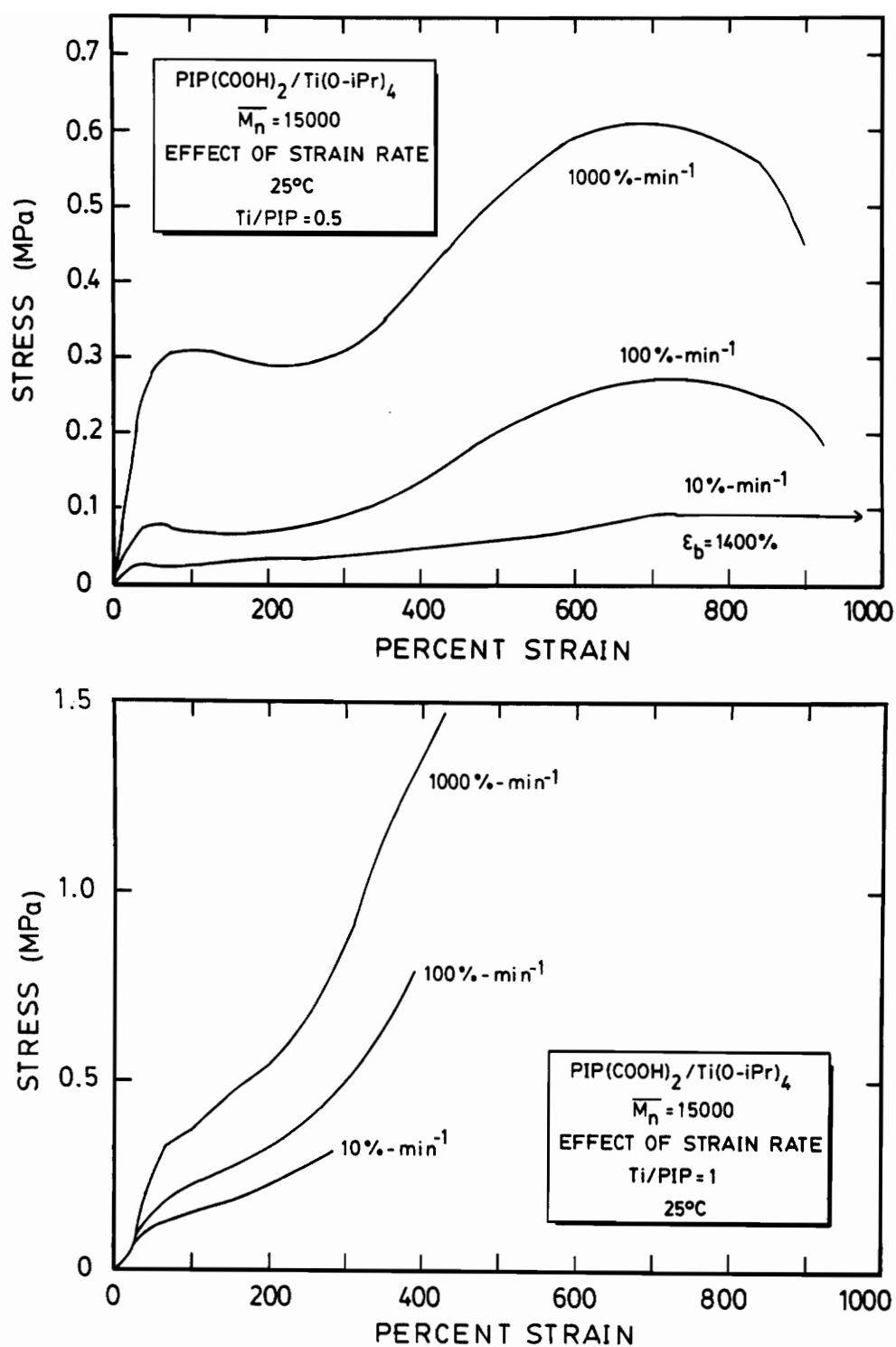


Figure 104. Effect of strain rate for materials with Ti/PIP ratios of 1/2 and 1.

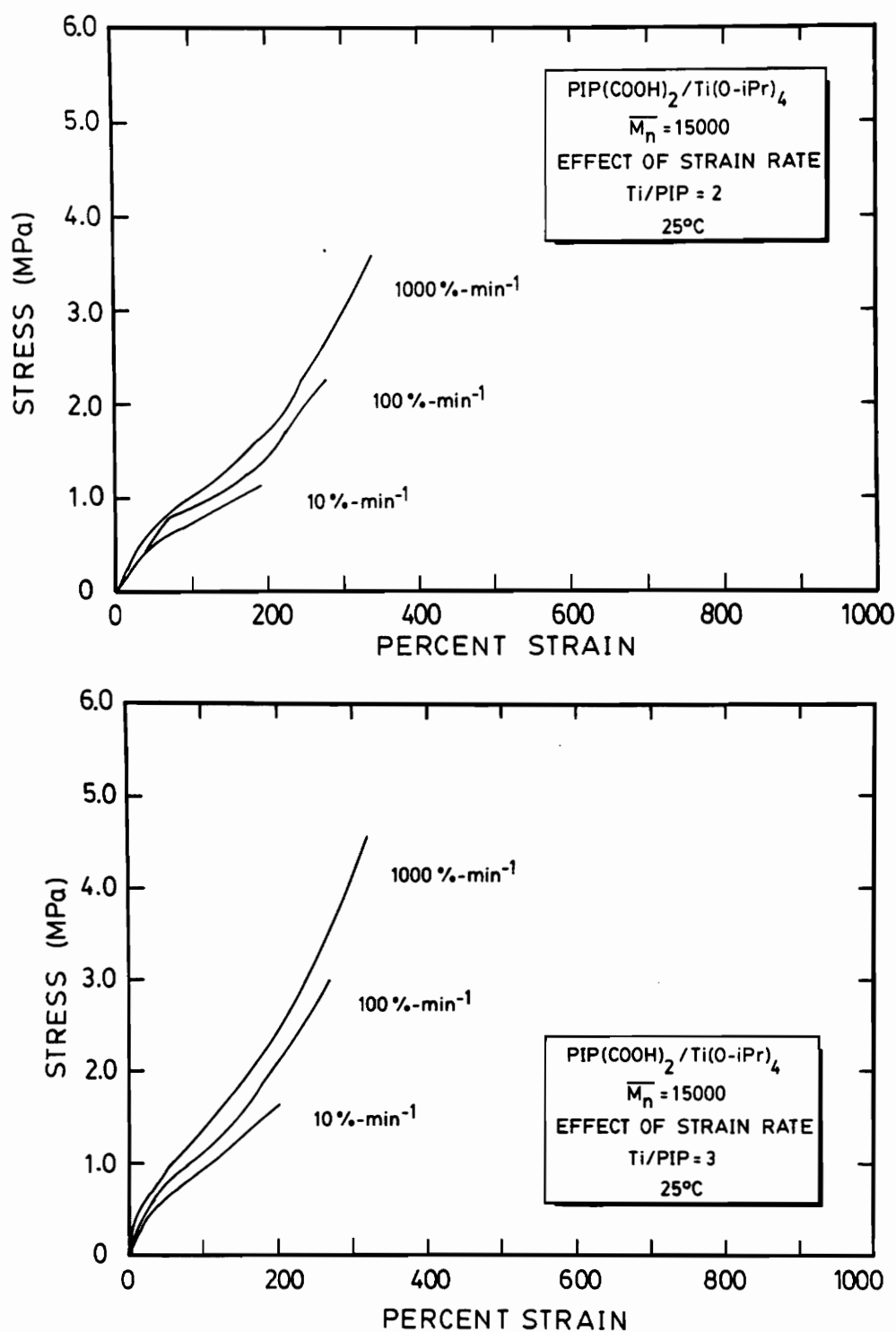


Figure 105. Effect of strain rate for materials with Ti/PIP ratios of 2 and 3.

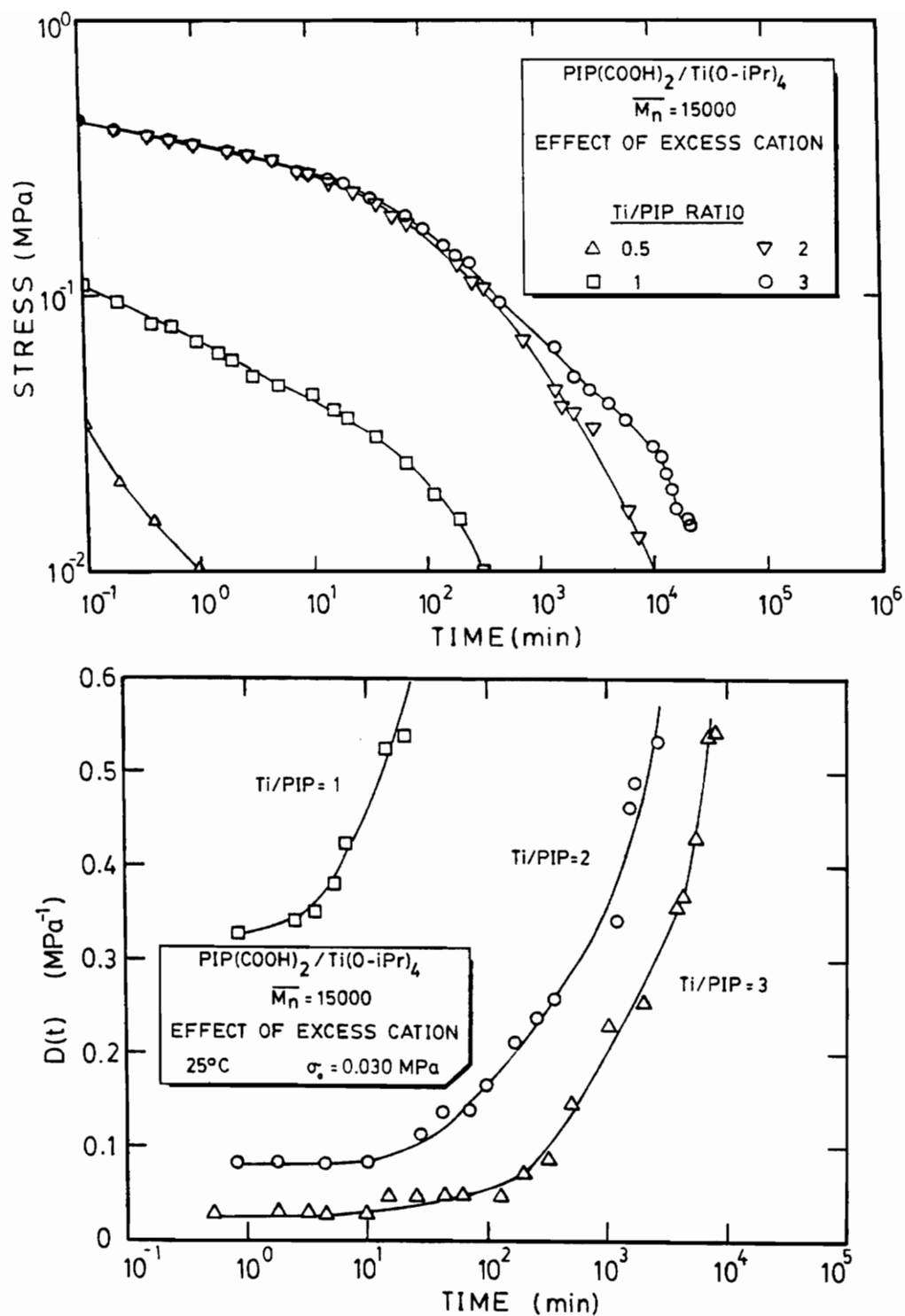


Figure 106. Stress relaxation and creep behavior of carboxy-telechelic polyisoprene neutralized with various amounts of titanium (IV).

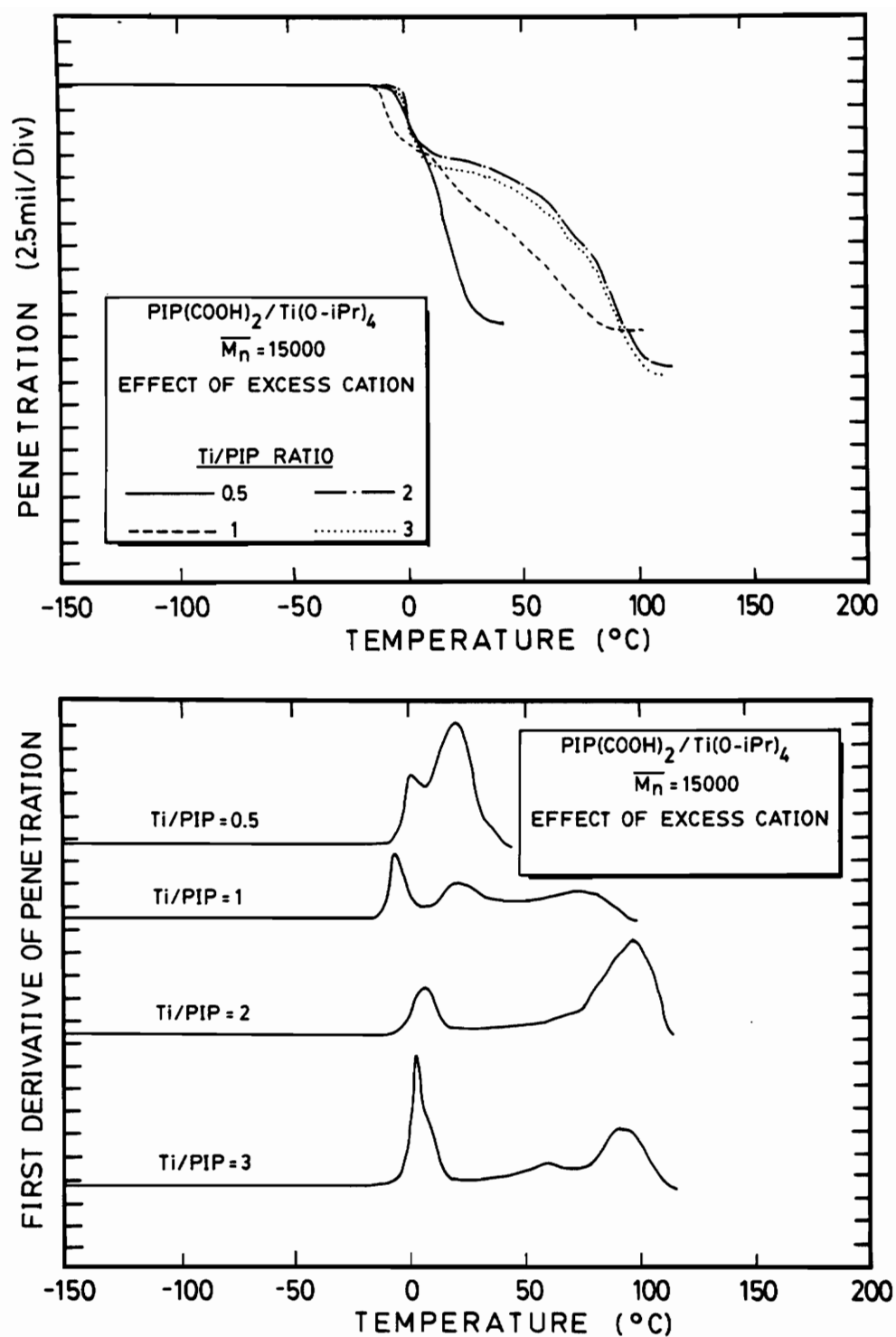


Figure 107. Thermomechanical behavior of carboxy-telechelic polyisoprene neutralized with various amounts of titanium (IV).

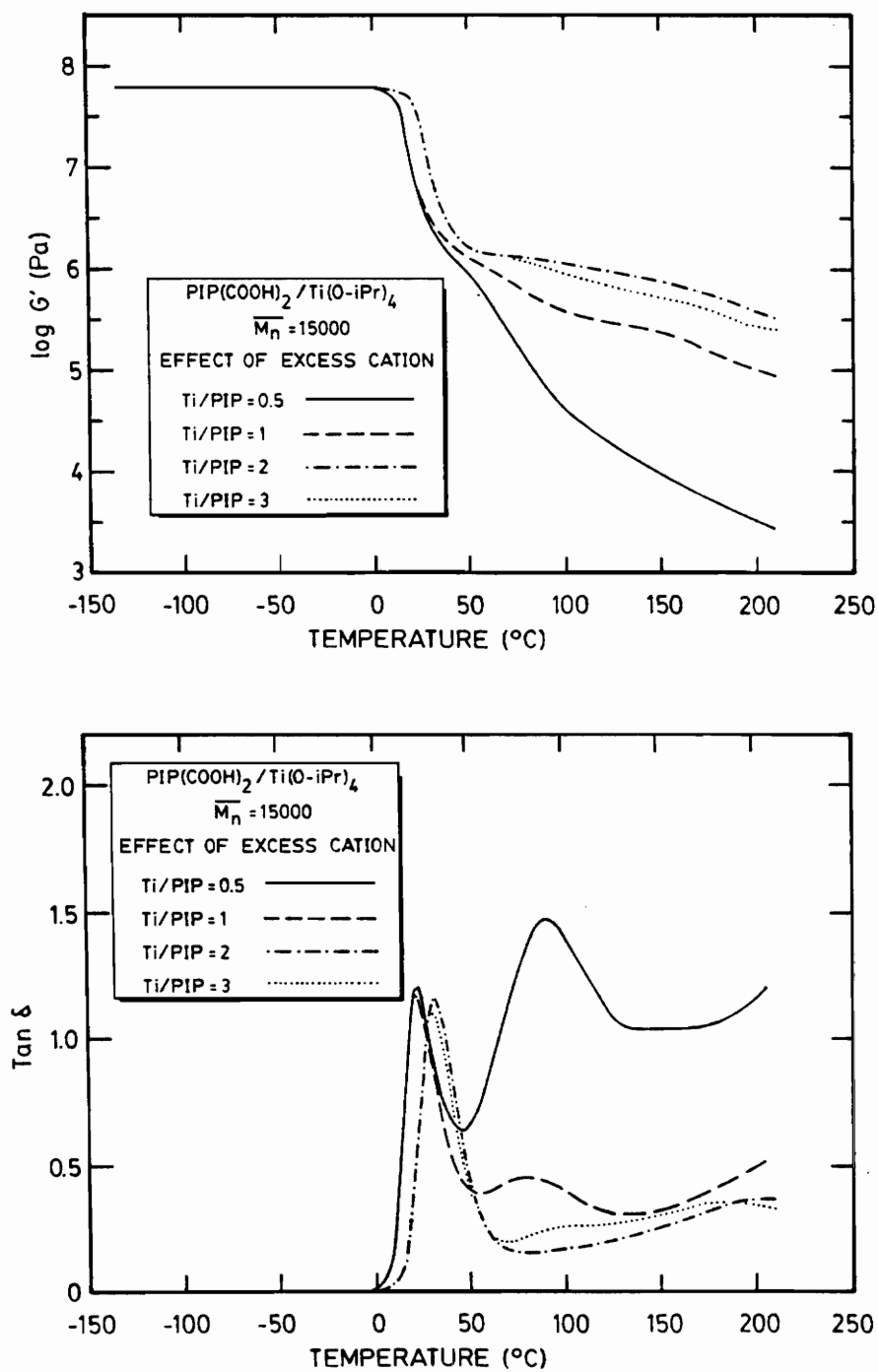


Figure 108. Dynamic mechanical behavior of carboxy-telechelic polyisoprene neutralized with various amounts of titanium (IV).

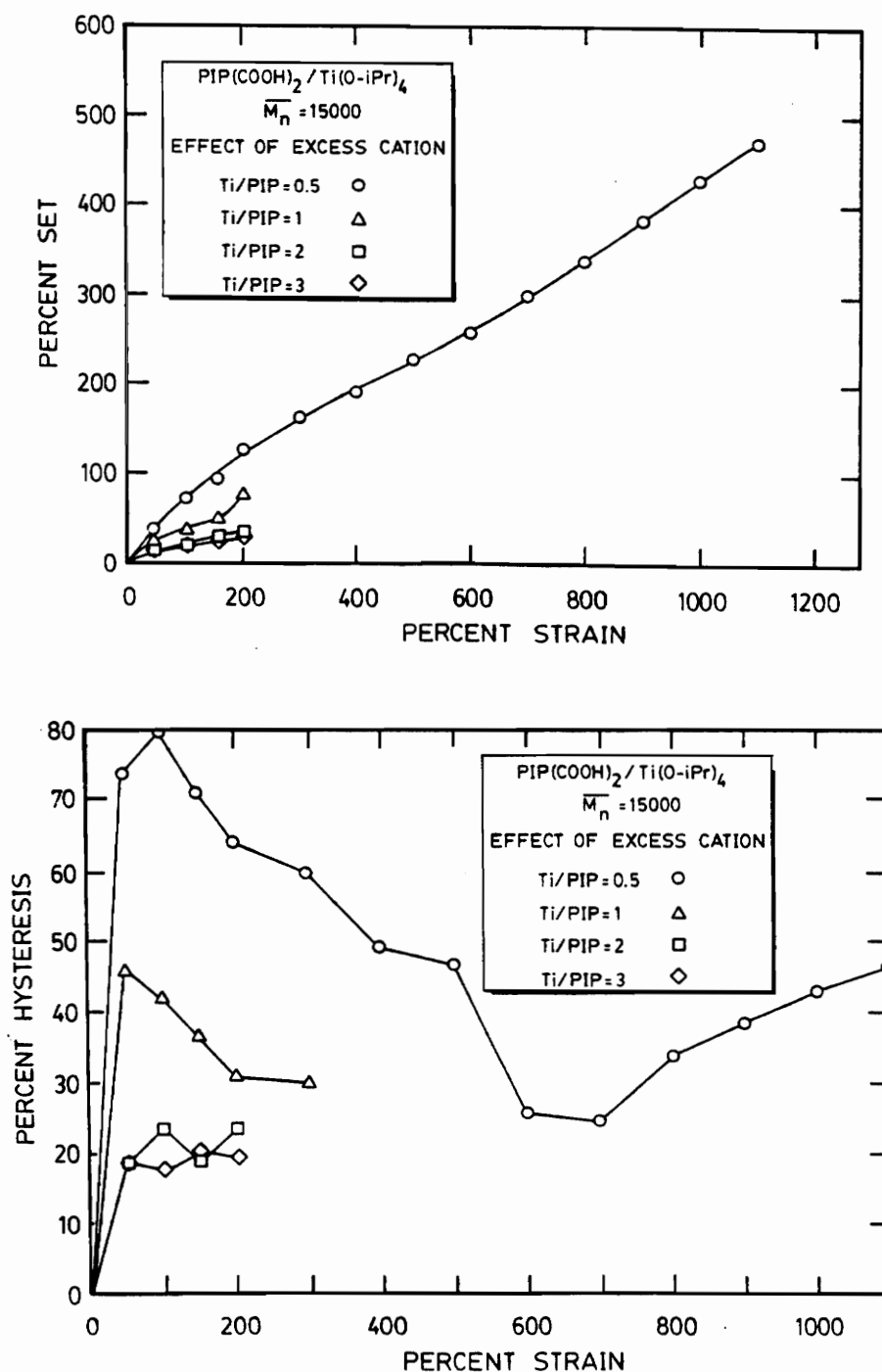


Figure 109. Instantaneous set and hysteresis of carboxy-telechelic polyisoprenes neutralized with various amounts of titanium (IV).

As with the carboxy-telechelic ionomers previously discussed, one further experiment was performed to check network stability. A sample of each was stretched to 100% strain and maintained at that strain for one week. The samples were then released and the recovery was monitored. The materials with Ti/PIP ratios of 2 and 3 broke within only three hours after stretching to 100% strain. The two materials with ratios of 1/2 and 1 were able to withstand the full week at 100% strain, but failed to recover at all following release. These results suggest that the network integrity of these materials, like the carboxy-telechelic materials previously discussed, is quite poor.

Mechanical Properties of Amine-Terminated Polybutadiene

Along with the carboxy-telechelic polyisoprenes provided by Professor Jérôme, a series of amine-terminated polybutadiene materials was also received. These materials were crosslinked with CuCl_2 , FeCl_3 , and NiCl_2 . Further details of exactly how the crosslinking occurs or experimental procedures used are not currently available. But one of the materials displayed a more stable network than any of the carboxylated elastomeric telechelic ionomers studied. These results are therefore reported here, although without full interpretation.

Figure 110 shows the stress-strain behavior of these materials at a strain rate of 100% per minute. Obviously, the material crosslinked with CuCl_2 possesses the strongest network, followed by FeCl_3 and NiCl_2 . Figure 111 shows the strain rate dependence of the stress-strain behavior for the materials crosslinked with CuCl_2 and FeCl_3 . These results again indicate that the CuCl_2 material forms a stronger network since its stress-strain behavior is less dependent upon strain rate. Finally, Figure 112 shows the stress relaxation and creep behavior of all three materials. Clearly, the

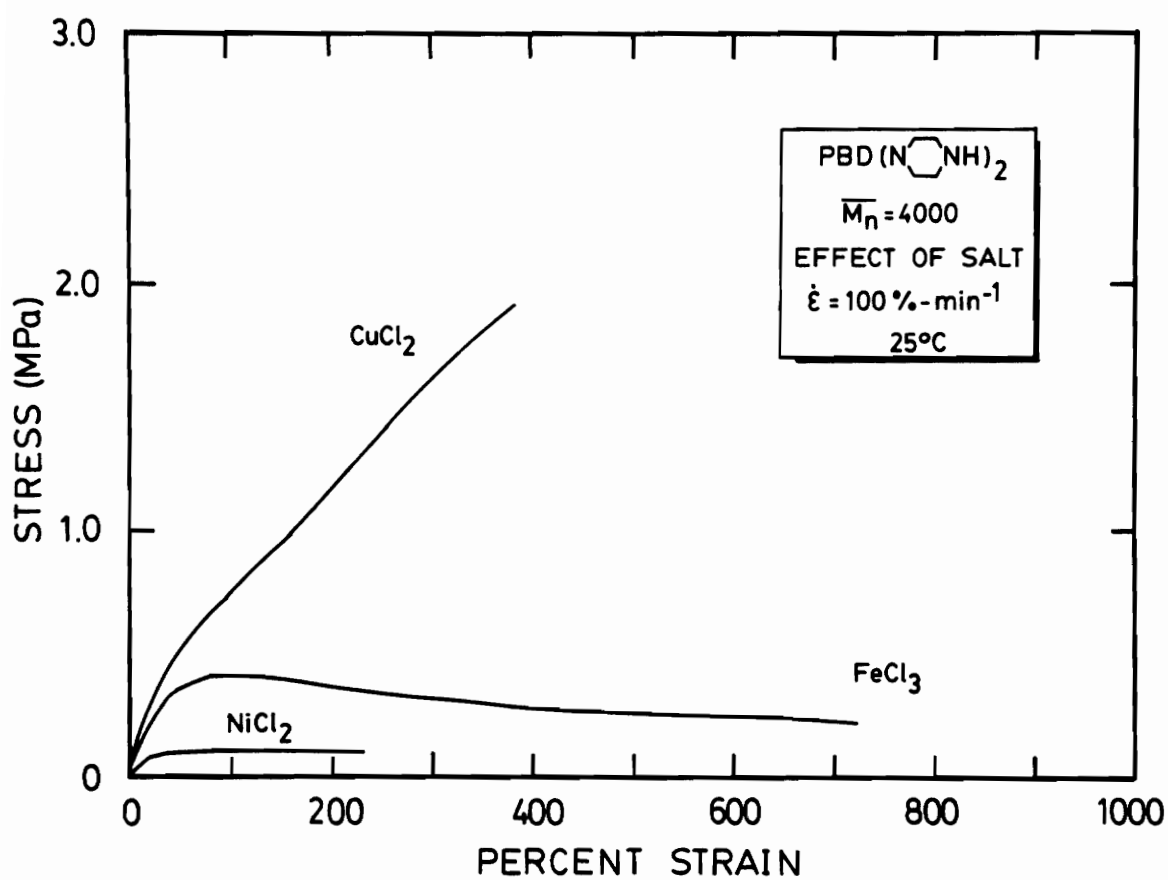


Figure 110. Stress-strain behavior of amine-terminated polybutadiene crosslinked with various chlorides.

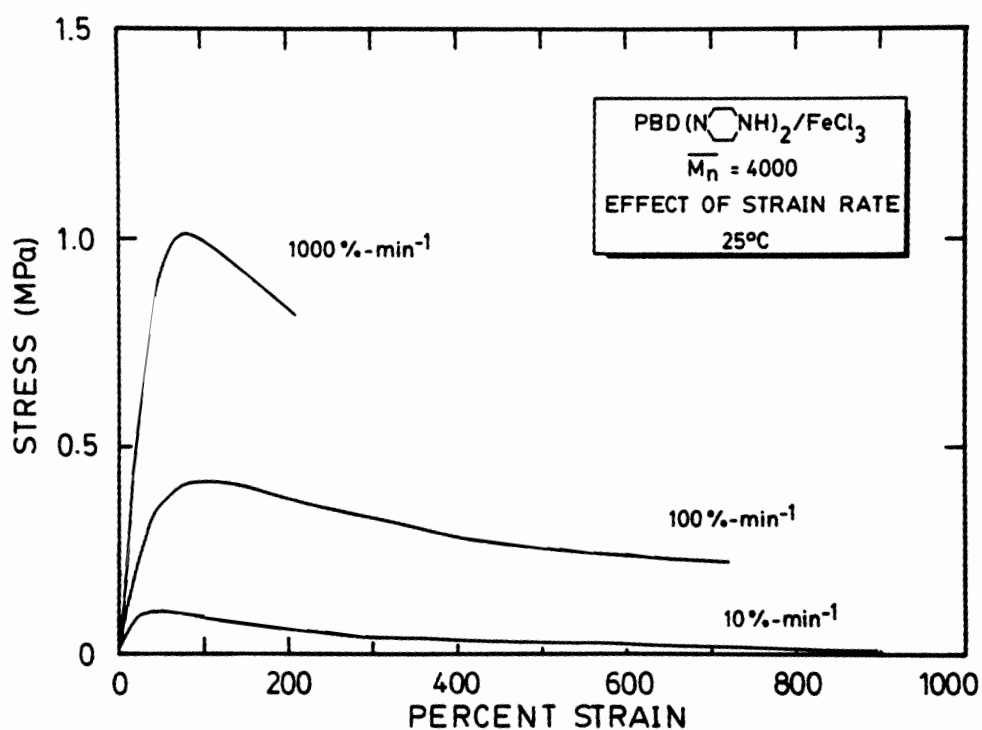
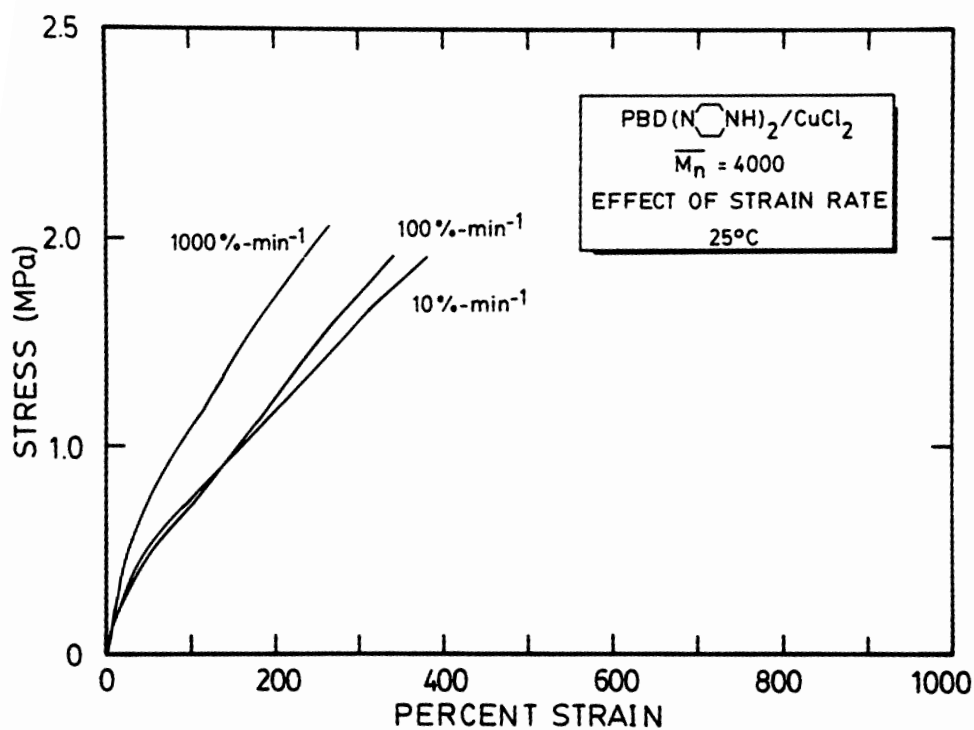


Figure 111. Effect of strain rate on behavior of materials neutralized with CuCl_2 and FeCl_3 .

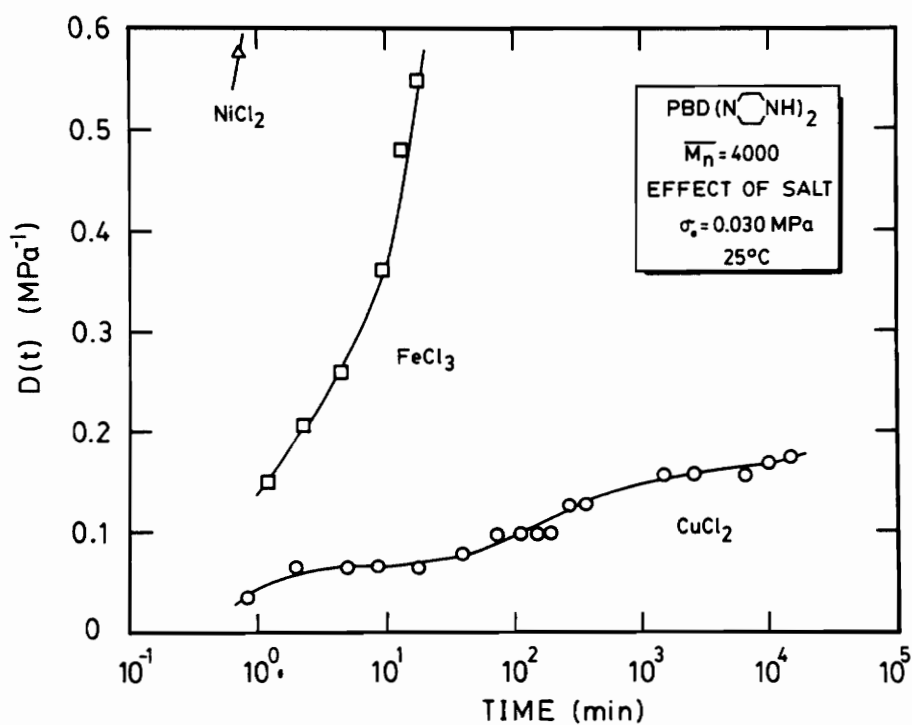
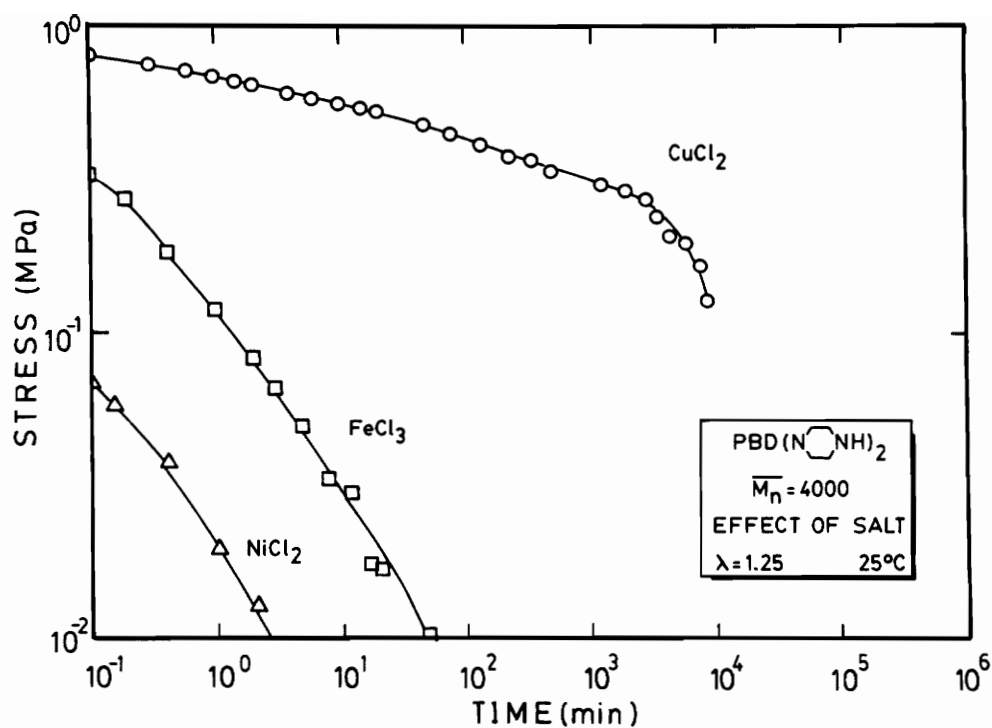


Figure 112. Stress relaxation and creep behavior of amine-terminated polybutadienes.

CuCl_2 material possesses a much more stable network than either of the other two materials.

As with the carboxy-telechelic polyisoprene materials discussed earlier, the long term network stability of these materials was further investigated by stretching samples to 100% strain, maintaining that strain for one week, and then monitoring recovery after releasing the sample. Recall that all of the carboxy-telechelic polyisoprene materials, except the one neutralized with K^+ , either fractured while strained or displayed no recovery after release. The K^+ material recovered only to 91% permanent set (or 9% of the 100% strain was recovered) after 10^4 minutes. While the amine-terminated polybutadiene materials crosslinked with FeCl_3 and NiCl_2 did not recover at all, the material crosslinked with CuCl_2 recovered to 55% permanent set (or 45% of the 100% strain was recovered) after 10^4 minutes. This is much more recovery than displayed by any of the carboxy-telechelic ionomers. The combination of strength and network stability for this material suggests that this method of crosslinking should certainly be investigated further.

Summary

The effect of molecular weight on stress-strain behavior of the carboxylated elastomeric telechelic ionomers was found to be dependent upon the type of cation used for neutralization. More strongly associating materials show higher stresses at lower molecular weights, while less strongly associating materials show the opposite trend. Mechanical properties were observed to be highly dependent upon the type (valence, ionic radius, ionic character, etc.) of neutralizing cation.

The carboxylated elastomeric telechelic ionomers obviously do not possess the high strength and good elastomeric character displayed by the sulfonated polyisobutylene

telechelic ionomers. However, it is possible that these materials might perform well as pressure-sensitive adhesives. It is well known that a pressure-sensitive adhesive must have suitable tack, which is the adhesive property closely related to initial bond formation with a surface upon brief contact under light pressure. Dahlquist [143] proposed that the compressive creep compliance on the time scale of the application (1 second) should be of the order of $10^{-7} \text{ cm}^2/\text{dyn}$ or larger. The Dahlquist criterion is thus given by

$$D(1s) \geq 10^{-7} \text{ cm}^2/\text{dyn} \quad (5.21)$$

If the compressive creep compliance at about 1 second is substantially less than $10^{-7} \text{ cm}^2/\text{dyn}$, tack will not be sufficient to initiate bonding since the material will not flow or creep quickly enough to intimately contact the substrate surface. Initial studies of the compressive creep compliance of these materials suggest that the Dahlquist criterion may be satisfied.

The amine-terminated polybutadiene crosslinked with CuCl_2 displayed relatively high strength and good network stability, while those crosslinked with FeCl_3 and NiCl_2 were quite weak and displayed poor network character. Although the crosslinking mechanism is not at all understood at present, the CuCl_2 material certainly deserves further study.

VI. Conclusions

This work on the structure-property behavior of elastomeric telechelic ionomers in bulk and solution has been concerned with three separate areas of study - (1) the bulk structure and properties of sulfonated polyisobutylene telechelic ionomers, (2) the solution behavior of sulfonated polyisobutylene telechelic ionomers, and (3) the bulk mechanical properties of carboxylated elastomeric telechelic ionomers. Studies in each of these three areas yielded interesting and valuable information about the behavior of ionomers in general and of elastomeric telechelic ionomers in particular. Since the work concerned three essentially different (but related) topics, the conclusions from each of these areas of study will be discussed separately.

Bulk Structure and Properties of Sulfonated Polyisobutylene Telechelic Ionomers

Small-angle x-ray scattering studies of the sulfonated polyisobutylene telechelic ionomers in bulk have revealed that the "ionic peak" commonly observed for ionomers, and which is often taken to be evidence of clustering, is observed only for low molecular weight materials. The peak has been observed only for materials below 10,000 \overline{M}_n . There was some evidence of a dependence of the peak on thermal history, but this effect could not be resolved because of sample limitations.

Long term stress relaxation and creep studies of these materials revealed that there are either two relaxation mechanisms or a single relaxation mechanism with a distrib-

ution that is skewed to longer times. At short times relaxation may occur primarily by rearrangement of the chains finally giving way to disruption of the ionic associations at long times. Thus these materials should not be considered for applications requiring the maintaining of a stress for long periods of time.

Neutralization of the sulfonated polyisobutylene telechelic ionomers with the cations Ce^{3+} and La^{3+} resulted in a more stable network than those formed from monovalent and divalent cations. This certainly must be due to the formation of trifunctional ionic network junction points and thus a higher ionic crosslink density

Solution Behavior of Sulfonated Polyisobutylene Telechelic Ionomers

The sulfonated polyisobutylene telechelic ionomers were observed to gel in nonpolar solvents such as hexane at concentrations as low as 1 to 2 g/dl. The gelation concentration was found to be lower for the trifunctional ionomer than for the difunctional ionomer of similar molecular weight due to its higher concentration of ionic groups as well as the presence of a permanent covalent network junction. However, when plotted vs. ionic concentration rather than polymer concentration, the gelation curves were found to coincide. For the trifunctional ionomers the gelation concentration decreases with increasing molecular weight, while the reverse trend was found for the difunctional ionomers. This result may be due to the low molecular weights of the difunctional species studied, i.e. \overline{M}_n of 6500 and 12000. It is possible that in this low molecular weight range the ionic content is more important than entanglements. Ionomers neutralized with potassium and calcium gel at about the same concentration, while those neutralized with zinc gel at a somewhat higher concentration due to the less ionic character of zinc. Excess neutralizing agent was found to slightly decrease the gelation concentration.

In nonpolar-polar solvent mixtures, an increase in relative viscosity is observed with increasing temperature. The viscosity increase is a function of both the concentration of the ionomer and the concentration of polar cosolvent. The molecular weight, and therefore the ionic content, was also found to be a factor.

The viscoelastic behavior of the sulfonated polyisobutylene telechelic ionomers in nonpolar solvents at relatively high concentrations (5-10 g/dl) is quite unusual. At low frequencies the G' and G'' curves for some solutions approach the limiting slopes expected for a linear viscoelastic fluid, while at higher frequencies G' may become constant indicating a network-like response. The linear difunctional materials are more likely to approach the limiting slopes in the terminal region as are materials neutralized with zinc rather than potassium, calcium, or cerium. Solutions of materials neutralized with potassium, calcium, or cerium display an essentially network-like response at room temperature over the entire experimentally accessible frequency range when the concentration is only 5 g/dl. The rubbery plateau is often observed to increase with increasing temperature much more than that expected from rubber elasticity effects. This may be due to increased mobility of the terminal ionic groups. The terminal region is also observed to shift to higher frequencies with increasing temperature, but the high-frequency transition to glass-like behavior remains at essentially the same frequency. When in a higher molecular weight solvent such as a paraffinic oil, the terminal region occurs at higher frequencies even with twice the concentration of polymer. This is apparently due to the decreased diffusion rate of the ionic groups in paraffin oil as compared to decalin. The G' and G'' modulus curves obtained at different temperatures are not superposable, and the solutions are thus thermorheologically complex.

Although the study of the steady shear behavior of these solutions was quite limited, they were found to be slightly shear thinning. At shear rates slightly above the onset of shear thinning the solutions were observed to fracture and thus render further data

meaningless. Shear thickening was not observed probably because shear thickening normally results from a transition from intramolecular association to intermolecular association. At the high concentrations studied the molecules were already highly intermolecularly associated.

Bulk Properties of Carboxylated Elastomeric Telechelic Ionomers

The effect of molecular weight on mechanical properties was found to be dependent upon the type of neutralizing cation. For a cation such as Ba^{2+} , increasing molecular weight in the range 15000-45000 \overline{M}_n increases resistance to deformation. Entanglements are therefore the controlling parameter. For similar materials neutralized with a fivefold excess of Zr^{4+} , the lower molecular weight material displays more resistance to deformation. Thus, in this case, as for the sulfonated polyisobutylene telechelic ionomers, the ionic crosslinks have more control over the behavior due to their greater strength. For a relatively constant molecular weight of 14500-15000, increasing the cation valence from 2 (Ba^{2+}) to 3 (Al^{3+}) to 4 (Zr^{4+}) increased the resistance to deformation.

Carboxy-telechelic polyisoprene of 15000 \overline{M}_n , neutralized with various cations from Groups IA and IIA of the periodic table and the first transition series resulted in materials with a wide range of properties. In general, for Group IA and Group IIA the stiffness of the material was found to increase with decreasing cation size as expected. The material neutralized with zinc displayed rather poor mechanical properties while that neutralized with nickel was much stronger. The strain rate dependence of stress-strain behavior gave a good indication of which cations were most effective at cross-linking the material. The most effective cations were sodium and magnesium. Stress relaxation and creep experiments indicated that these cations also formed the most stable networks.

The series of carboxy-telechelic polyisoprene materials neutralized with various amounts of Ti^{4+} also displayed a very wide range of mechanical properties. It was determined that at least four times the stoichiometric amount of Ti^{4+} is necessary to effectively crosslink the material.

The carboxylated elastomeric telechelic ionomers do not possess the good elastomeric properties displayed by the sulfonated polyisobutylene telechelic ionomers. Even though in stress-strain tests the carboxylated elastomeric telechelic ionomers may reach the stresses reached by the sulfonated polyisobutylene telechelic ionomers, other experiments such as permanent set and hysteresis reveal that their network stability and recoverability are not nearly as good.

The amine-terminated material crosslinked with CuCl_2 displays relatively high strength and good network stability, but those crosslinked with FeCl_3 and NiCl_2 have quite poor properties. The mechanism of the crosslinking is not currently understood, but the properties of the CuCl_2 material suggests that further study is warranted.

VII. Recommendations for Further Study

This research has been directed at obtaining a better understanding of the behavior of ionomers, particularly elastomeric telechelic ionomers, in both bulk and solution. Although the results of the work have certainly been interesting and enlightening, they have by no means provided all of the answers. In fact, as most research does, it has brought up many important and difficult questions. Of course, these questions can only be answered through further research. Some ideas for potential fruitful areas for future research are discussed here.

Bulk Structure and Properties of Sulfonated Polyisobutylene Telechelic Ionomers

Further studies of these materials by small-angle x-ray scattering are certainly warranted. Although the "ionic peak" is clearly present for materials below 10,000 \overline{M}_n , there is still some question of its dependence upon thermal history. Studies should be conducted to provide an understanding of any aging behavior. Concurrent mechanical property studies should also be conducted to determine if the changing morphology (if it is changing) affects mechanical properties. Further studies should also be done as a function of molecular weight to better define the molecular weight at which the peak appears. It would also be interesting to perform an electron spin resonance study on materials of various molecular weights, neutralized with a paramagnetic cation, to determine how this variable affects the *average* number of ionic groups per multiplet. It

might be expected that as molecular weight decreases, and ionic content thus increases, the number of ionic groups per multiplet should increase.

The long term stress relaxation and creep experiments were conducted in a laboratory atmosphere in which temperature and humidity could not be controlled. Although it is doubtful that atmospheric moisture was absorbed in sufficient amounts to affect the ionic associations, it would be of interest to perform similar experiments in a dry environment to be certain of this conclusion.

Although the sulfonated polyisobutylene telechelic ionomers were successfully neutralized with Ce^{3+} and La^{3+} , other cations could not be studied due to the small amount of material available. It would certainly be desirable to attempt neutralization with other trivalent as well as tetravalent cations and investigate the properties of the resulting materials.

It would be interesting to compare the mechanical properties of these sulfonated polyisobutylene telechelic ionomers with those of similar carboxylated materials. The comparison of sulfonated vs. carboxylated ionomers might be more interesting for telechelic elastomers than for random glassy ionomers, with which the comparison has previously been made.

Solution Behavior of Sulfonated Polyisobutylene Telechelic Ionomers

One of the primary questions regarding the solution behavior of the sulfonated polyisobutylene telechelic ionomers concerns the molecular weight dependence of the gelation concentration in nonpolar solvents for the linear difunctional species. Previous work on carboxylated elastomeric telechelic ionomers showed an $\overline{M}_n^{-1/2}$ dependence of the gelation concentration, i.e. gelation concentration decreases with increasing molecular weight. Of course, the results on linear sulfonated polyisobutylene telechelic

ionomers with \overline{M}_n 's of 6500 and 12000 show the reverse trend, possibly because of the low molecular weight range. A broader series of molecular weights should be prepared, extending from about 4000 to 25000 \overline{M}_n to determine if there is a critical molecular weight at which ionic concentration becomes more important than entanglements.

It was found that if the gelation curves for D-12-K-0 and T-11-K-0 are plotted as a function of ionic concentration they coincide. It would be of interest to conduct a similar study of difunctional and trifunctional species at various molecular weights to determine if this is a general result or if it was fortuitous for this molecular weight region.

Further theoretical and experimental work should be done to gain a better understanding of the temperature-dependent equilibrium between the polar cosolvent, the nonpolar solvent, and the ionic groups on the polymer chain. This is a complex problem, but it certainly appears to be one worthy of further effort.

The thermorheological complexity of concentrated solutions of the sulfonated polyisobutylene telechelic ionomers seems to be unusual for ionomer solutions. Also the large increases in the plateau modulus with increasing temperature have not been observed before. It would be of interest to conduct similar studies on a higher molecular weight elastomeric ionomer with enough randomly distributed ionic groups to give about the same concentration of ionic groups present in the telechelic ionomers. This would help to determine whether or not this effect is due to the terminal location of the ionic groups where they should have greater mobility and thus a higher probability of contacting other ionic groups with which to associate. It might be possible to obtain more information on the dynamics of the ionic associations by performing dynamic experiments such as stress growth and constrained recoil.

Further studies should be done on the steady shear behavior of these solutions. Since the high concentration solutions were observed to fracture at intermediate shear rates, studies should be done on lower concentration solutions to investigate the possi-

bility of observing the shear thickening behavior that other telechelic ionomers have displayed. In fact, solutions of lower concentration should be more likely to display shear thickening since shear thickening normally occurs due to a transition from intramolecular association to intermolecular association. Intramolecular association would certainly be expected to increase as concentration is decreased.

Bulk Properties of Carboxylated Elastomeric Telechelic Ionomers

Although the network stability and recoverability of the carboxylated elastomeric telechelic ionomers are quite poor compared to the sulfonated polyisobutylene telechelic ionomers, they may have some potential as adhesives. This possibility should certainly be explored.

The amine-terminated polybutadiene material crosslinked with CuCl_2 displayed both relatively high strength and good network stability. The mechanism of this crosslinking effect should be studied, as should the further use of this type of interaction to crosslink polymers.

References

1. M. R. Tant and G. L. Wilkes, *J. Macromol. Sci. - Rev. Macromol. Chem. Phys.*, in press.
2. W. J. MacKnight and T. R. Earnest, *J. Polym. Sci. - Macromol. Rev.* **16**, 41 (1981).
3. C. G. Banzuin and A. Eisenberg, *Ind. Eng. Chem. Prod. Res. Dev.* **20**, 271 (1981).
4. R. Longworth, in *Developments in Ionic Polymers - I*, A.D. Wilson and H. J. Prosser, Eds., Applied Science, Essex, England, 1984.
5. K. A. Mauritz and A. J. Hopfinger, in *Modern Aspects of Electrochemistry*, J. O'M. Bockris, B. E. Conway, and R. E. White, Eds., Plenum, New York, 1982.
6. H. P. Brown, US Patent 2626248, January 1953.
7. E. P. Otocka, M. Y. Hellman, and L. L. Blyler, *J. Appl. Phys.* **40**, 4221 (1969).
8. K. K. S. Hwang, C. Z. Yang, and S. L. Cooper, *Polym. Eng. Sci.* **21**, 1027 (1981).
9. A. Eisenberg, *Macromolecules* **3**, 2 (1970).
10. R. Longworth, in *Ionic Polymers*, L. Holliday, Ed., Halsted-Wiley, New York, 1975.
11. R. Longworth and D. J. Vaughan, *Polym. Prepr.* **9**, 525 (1968).
12. C. L. Marx, D. F. Caulfield, and S. L. Cooper, *Macromolecules* **6**, 344 (1973).
13. F. L. Binsbergen and G. F. Kroon, *Macromolecules* **6**, 145 (1973).
14. W. J. MacKnight, W. P. Taggart, and R. S. Stein, *J. Polym. Sci. Polym. Symp.* **45**, 113 (1974).
15. G. Porod, *Kolloid Z.* **124**, 83 (1951).
16. A. Guinier and G. Fournet, *Small Angle Scattering of X-Rays*, Wiley, New York, 1955.

17. M. Pineri, C. T. Meyer, A. M. Levelut, and M. Lambert, *J. Polym. Sci. Polym. Phys. Ed.* **12**, 115 (1974).
18. C. T. Meyer and M. Pineri, *J. Polym. Sci. Polym. Phys. Ed.* **13**, 1057 (1975).
19. M. Pineri, C. T. Meyer, and A. Bourret, *J. Polym. Sci. Polym. Phys. Ed.* **13**, 1881 (1975).
20. C. T. Meyer and M. Pineri, *J. Polym. Sci. Polym. Phys. Ed.* **16**, 569 (1978).
21. M. Fujimura, T. Hashimoto, and H. Kawai, *Macromolecules* **15**, 136 (1982).
22. D. J. Yarusso and S. L. Cooper, *Macromolecules* **16**, 1871 (1983).
23. D. J. Yarusso and S. L. Cooper, *Polymer* **26**, 371 (1985).
24. W. C. Forsman, *Macromolecules* **15**, 1032 (1982).
25. W. C. Forsman, W. J. MacKnight, and J. S. Higgins, *Macromolecules* **17**, 490 (1984).
26. B. Dreyfus, *Macromolecules* **18**, 284 (1985).
27. B. Dreyfus, in *Coulombic Interactions in Macromolecular Systems*, A. Eisenberg and F. E. Bailey, Eds., American Chemical Society Symposium Series #302 (1986).
28. P. C. Painter, B. A. Brozoski, and M. M. Coleman, *J. Polym. Sci. Polym. Phys. Ed.* **20**, 1069 (1982).
29. B. A. Brozoski, M. M. Coleman, and P. C. Painter, *J. Polym. Sci. Polym. Phys. Ed.* **21**, 301 (1983).
30. B. A. Brozoski, M. M. Coleman, and P. C. Painter, *Macromolecules* **17**, 230 (1984).
31. V. D. Mattern, Jr. and W. M. Risen, Jr., *J. Polym. Sci. Polym. Phys. Ed.* **22**, 67 (1984).
32. D. G. Peiffer, B. L. Hager, R. A. Weiss, P. K. Agarwal, and R. D. Lundberg, *J. Polym. Sci. Polym. Phys. Ed.* **23**, 1869 (1985).
33. A. Neppel, I. S. Butler, and A. Eisenberg, *J. Polym. Sci. Polym. Phys. Ed.* **17**, 2145 (1979).
34. A. Neppel, I. S. Butler, and A. Eisenberg, *Macromolecules* **12**, 948 (1979).
35. A. Neppel, I. S. Butler, and A. Eisenberg, *J. Canadian de Chemie* **57**, 2518 (1979).
36. H. K. Pan, G. S. Knapp, and S. L. Cooper, *Coll. Polym. Sci.* **262**, 734 (1984).

37. Y. S. Ding, D. J. Yarusso, H. K. D. Pan, and S. L. Cooper, *J. Appl. Phys.* **56**, 2396 (1984).
38. H. K. Pan, A. Meagher, M. Pineri, G. S. Knapp, and S. L. Cooper, *J. Chem. Phys.* **82**, 1529 (1985).
39. H. Toriumi, R. A. Weiss, and H. A. Frank, *Macromolecules* **17**, 2104, (1984).
40. D. L. Handlin, W. J. MacKnight, and E. L. Thomas, *Macromolecules* **14**, 795 (1981).
41. M. Drzewinski and W. J. MacKnight, *J. Appl. Polym. Sci.* **30**, 4753 (1985).
42. Y. Nakano and W. J. MacKnight, *Macromolecules* **17**, 1585 (1984).
43. M. Hara, private communication.
44. H. Matsuura and A. Eisenberg, *J. Polym. Sci. Polym. Phys. Ed.* **14**, 1201 (1976).
45. A. Eisenberg, H. Matsuura, and T. Yokoyama, *J. Polym. Sci. Part A* **29**, 2131 (1971).
46. R. Jérôme, J. Horrion, R. Fayt, and Ph. Teyssié, *Macromolecules* **17**, 2447 (1984).
47. E. Besso, R. Legras, A. Eisenberg, F. W. Harris, A. E. Steck, and H. L. Yeager, *J. Appl. Polym. Sci.* **30**, 2821 (1985).
48. P. K. Agarwal, H. S. Makowski, and R. D. Lundberg, *Macromolecules* **13**, 1679 (1980).
49. W. J. MacKnight, L. W. McKenna, and B. E. Read, *J. Appl. Phys.* **38**, 4208 (1967).
50. A. Eisenberg, H. Matsuura, and T. Tsutsui, *J. Polym. Sci. Polym. Phys. Ed.* **18**, 479 (1980).
51. T. C. Ward and A. V. Tobolsky, *J. Appl. Polym. Sci.* **11**, 2403 (1967).
52. R. W. Rees and D. J. Vaughan, *Polym. Prepr.* **6**, 296 (1965).
53. T. Smith and W. Chu, *J. Polym. Sci. B2* **10**, 133 (1972).
54. A. Eisenberg and M. Navratil, *J. Polym. Sci. Polym. Lett. Ed.* **10**, 537 (1972).
55. A. Eisenberg and M. Navratil, *Macromolecules* **6**, 604 (1973).
56. M. Navratil and A. Eisenberg, *Macromolecules* **7**, 84 (1974).
57. R. A. Weiss and J. A. Lefelar, *Polymer* **27**, 3 (1986).

58. R. D. Lundberg and H. S. Makowski, in *Ions in Polymers*, A. Eisenberg, Ed., Adv Chem. Ser. #187, American Chemical Society, Washington, D.C., Chapter 2, 1980.
59. S. Granick, *J. Appl. Polym. Sci.* **28**, 1717 (1983).
60. I. Duvedvani, R. D. Lundberg, C. Wood-Cordova, and G.L. Wilkes, in *Coulombic Interactions in Macromolecular Systems*, A. Eisenberg and F. E. Bailey, Eds. ACS Symp. Ser. 302, Chapter 15, 1986.
61. F. C. Wilson, R. Longworth, and D. J. Vaughan, *Polym. Prepr.* **9** (1), 505 (1968).
62. A. Moudden, A. M. Levelut, and M. Pineri, *J. Polym. Sci. Polym. Phys. Ed.* **15**, 1707 (1977).
63. G. Broze, R. Jérôme, Ph. Teyssié, and B. Gallot, *J. Polym. Sci. Polym. Lett. Ed.* **19**, 415 (1981).
64. R. A. Weiss, J. Lefelar, and H. Toriumi, *J. Polym. Sci. Polym. Lett. Ed.* **21**, 661 (1983).
65. R. D. Lundberg and R. R. Phillips, *J. Polym. Sci. Polym. Lett. Ed.* **22**, 377 (1984).
66. H. P. Brown, *Rubber Chem. Technol.* **30**, 1347 (1957).
67. H. P. Brown and N. G. Duke, *Rubber World* **130**, 784 (1954).
68. H. P. Brown, *Rubber Chem. Technol.* **36**, 931 (1963).
69. D. K. Jenkins and E. W. Duck, in *Ionic Polymers*, L. Holliday, Ed., Halsted-Wiley, New York, 1975.
70. N. H. Canter, U.S. Patent 3870841 (1978).
71. C. P. O. Farrel and G. E. Jernick, U. S. Patent 3836511 (1974).
72. H. S. Makowski, R. D. Lundberg, and G. S. Singhal, U.S. Patent 3870841 (1975).
73. H. S. Makowski, R. D. Lundberg, L. Westerman, and J. Bock, in *Ions in Polymers*, A. Eisenberg, Ed., Adv Chem. Ser. 187, American Chemical Society, Washington, D.C., Chapter 1, 1980.
74. H. S. Makowski and R. D. Lundberg, in *Ions in Polymers*, A. Eisenberg, Ed., Adv. Chem. Ser. 187, American Chemical Society, Washington, D.C., Chapter 1, 1980.
75. G. Broze, R. Jérôme, Ph. Teyssié, and C. Marco, *Polym. Bull.* **4**, 241 (1981).

76. G. Broze, R. Jérôme, Ph. Teyssié, and C. Marco, *J. Polym. Sci. Polym. Phys. Ed.* **21**, 2205 (1983).
77. G. Broze, R. Jérôme, Ph. Teyssié, and C. Marco, *Macromolecules* **16**, 1771 (1983).
78. G. Broze, R. Jérôme, and Ph. Teyssié, *J. Polym. Sci. Polym. Lett. Ed.* **21**, 237 (1983).
79. G. Broze, R. Jérôme, Ph. Teyssié, and C. Marco, *Macromolecules* **18**, 1376 (1985).
80. R. Jérôme and G. Broze, *Rubber Chem. Technol.* **58**, 223 (1985).
81. M. Laleg, Y. Camberlin, G. Boiteus-Steffan, G. Seytre, and J. P. Pascault, *J. Macromol. Sci. - Phys.* **B23**, 233 (1984).
82. Y. Mohajer, D. Tyagi, G. L. Wilkes, R. F. Storey, and J. P. Kennedy, *Polym. Bull.* **8**, 47 (1982).
83. S. Bagrodia, Y. Mohajer, G. L. Wilkes, R. F. Storey, and J. P. Kennedy, *Polym. Bull.* **8**, 281 (1982).
84. S. Bagrodia, Y. Mohajer, G. L. Wilkes, R. F. Storey, and J. P. Kennedy, *Polym. Bull.* **9**, 174 (1983).
85. Y. Mohajer, S. Bagrodia, G. L. Wilkes, R. F. Storey, and J. P. Kennedy, *J. Appl. Polym. Sci.* **29**, 1943 (1984).
86. S. R. Bagrodia, G. L. Wilkes, and J. P. Kennedy, *J. Appl. Polym. Sci.* **30**, 2179 (1985).
87. S. Bagrodia, R. Pisipati, G. L. Wilkes, R. F. Storey, and J. P. Kennedy, *J. Appl. Polym. Sci.* **29**, 3065 (1984).
88. S. Bagrodia, G. L. Wilkes, and J. P. Kennedy, *Polym. Eng. Sci.* **26**, 62 (1986).
89. S. Bagrodia, M. R. Tant, G. L. Wilkes, and J. P. Kennedy, *Polymer*, submitted.
90. K. Sato, *Rubber Chem. Technol.* **56**, 942 (1983).
91. J. A. Miller, K. K. S. Hwang, and S. L. Cooper, *J. Macromol. Sci. - Phys.* **B22**, 321 (1983).
92. K. K. S. Hwang, C. Z. Yang, J. A. Miller, and S. L. Cooper, *IUPAC 28th Macromol. Symp.*, p. 900 (1982).
93. K. K. S. Hwang, T. A. Speckhard, and S. L. Cooper, *J. Macromol. Sci. - Phys.* **B23**, 153 (1984).

94. T. A. Speckhard, K. K. S. Hwang, C. Z. Yang, W. R. Laupan, and S. L. Cooper, *J. Macromol. Sci. - Phys.* **B23**, 175 (1984).
95. M. Rutkowska and A. Eisenberg, *Macromolecules* **17**, 822 (1984).
96. M. Rutkowska and A. Eisenberg, *J. Appl. Polym. Sci.* **29**, 755 (1984).
97. M. Rutkowska and A. Eisenberg, *J. Appl. Polym. Sci.* **30**, 3317 (1985).
98. R. W. Conelly, R. C. McKonkey, J. M. Noonan, and G. H. Pearson, *J. Polym. Sci. Polym. Phys. Ed.* **20**, 259 (1982).
99. P. Smith and A. Eisenberg, *J. Polym. Sci. Polym. Lett. Ed.* **21**, 223 (1983).
100. Z-L. Zhou and A. Eisenberg, *J. Polym. Sci. Polym. Phys. Ed.* **21**, 595 (1983).
101. M. Hara and A. Eisenberg, *Macromolecules* **17**, 1335 (1984).
102. A. Eisenberg and M. Hara, *Polym. Eng. Sci.* **24**, 1306 (1984).
103. D. Dietrich, *Prog. Org. Coatings* **9**, 281 (1981).
104. R. D. Lundberg, in *Structure and Properties of Ionomers*, in press.
105. R. D. Lundberg and R. R. Phillips, *J. Polym. Sci. Polym. Phys. Ed.* **20**, 1143 (1982).
106. G. Broze, R. Jérôme, and Ph. Teyssié, *Macromolecules* **14**, 224 (1981).
107. G. Broze, R. Jérôme, and Ph. Teyssié, *Macromolecules* **15**, 920 (1982).
108. G. Broze, R. Jérôme, and Ph. Teyssié, *Macromolecules* **15**, 1300 (1982).
109. J. F. Joanny, *Polymer* **21**, 71 (1980).
110. W. C. Forsman and S. Hong, *Polym. Prepr.* **25** (2), 305 (1984).
111. W. C. Forsman and S. Hong, in *Structure and Properties of Ionomers*, in press.
112. D. G. Peiffer and R. D. Lundberg, *J. Polym. Sci. Polym. Chem. Ed.* **22**, 1757 (1984).
113. J. Niezette, J. Vanderschueren, and L. Aras, *J. Polym. Sci. Polym. Phys. Ed.* **22**, 1845 (1984).
114. C. Rochas, A. Domard, and M. Rinaudo, *Polymer* **20**, 76 (1979).
115. R. D. Lundberg and H. S. Makowski, *J. Polym. Sci. Polym. Phys. Ed.* **18**, 1821 (1980).
116. R. D. Lundberg, *J. Appl. Polym. Sci.* **27**, 4623 (1982).

117. R. D. Lundberg, *J. Appl. Polym. Sci.*, in press.
118. N. Misra and B. M. Mandal, *Macromolecules* **17**, 495 (1984).
119. P. K. Agarwal and R. D. Lundberg, *Macromolecules* **17**, 1918 (1984).
120. P. K. Agarwal and R. D. Lundberg, *Macromolecules* **17**, 1928 (1984).
121. P. K. Agarwal, R. T. Garner, and R. D. Lundberg, *Macromolecules* **17**, 2794 (1984).
122. G. Broze, R. Jérôme, Ph. Teyssié, and C. Marco, *Macromolecules* **16**, 996 (1983).
123. T. A. Witten, Jr. and M. H. Cohen, *Macromolecules* **18**, 1915 (1985).
124. A. E. Gonzalez, *Polymer* **24**, 77 (1983).
125. A. E. Gonzalez, *Polymer* **25**, 1469 (1984).
126. J. P. Kennedy, S. Y. Huang, and S. C. Feinberg, *J. Polym. Sci. Polym. Lett. Ed.* **15**, 2869 (1977).
127. J. P. Kennedy and R. A. Smith, *J. Polym. Sci. Polym. Chem. Ed.* **18**, 1523 (1980).
128. J. P. Kennedy, L. R. Ross, J. E. Lackey, and O. Nuyken, *Polym. Bull.* **4**, 67 (1981).
129. J. P. Kennedy, V. S. C. Chang, R. A. Smith, and B. Ivan, *Polym. Bull.* **1**, 57 (1979).
130. J. P. Kennedy and R. F. Storey, *Org. Coat. Appl. Polym. Sci.* **46**, 182 (1982).
131. J. P. Kennedy and R. F. Storey, *IUPAC 28th Macromol. Symp.*, p. 905 (1982).
132. R. F. Storey, Ph.D. Dissertation, The University of Akron, Akron, Ohio (1983).
133. C. W. Strobel, U.S. Patent 3287344 (1966).
134. J. G. Zilliox, *Makrom. Chem.* **156**, 121 (1972).
135. S. Bywater, *Adv. Polym. Sci.* **30**, 89 (1979).
136. S. Bagrodia, Ph.D. Dissertation, Virginia Polytechnic Institute and State University, Blacksburg, 1984.
137. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, p. 310.
138. R. A. Weiss, private communication.

- 139. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1980, Chapter 9.
- 140. M. Reiner, *Phys. Today* 17 (1), 62 (1964).
- 141. G. Broze, R. Jérôme, Ph. Teyssié, and B. Gallot, *J. Polym. Sci. Polym. Lett. Ed.* 19, 415 (1981).
- 142. J. Ledent, F. Fontaine, H. Reynaers, and R. Jérôme, *Polym. Bull.* 14, 461 (1985).
- 143. C. A. Dahlquist, *Tack and Adhesion: Fundamentals and Practice*, McLaren & Sons, Ltd., London, 1966.

VITA

Martin Ray Tant, son of Mr. and Mrs. Larry R. Tant of Poquoson, Virginia, was born on April 10, 1953 in Seneca, South Carolina. After growing up in Seneca and Clemson, South Carolina and Hampton, Virginia, he graduated from Bethel High School in Hampton in 1971. He then entered Old Dominion University and was awarded the degree of Bachelor of Science in Chemistry in May 1975. After working as a chemist with the Naval Mine Engineering Facility in Yorktown, Virginia, he entered the graduate program in chemical engineering at Virginia Polytechnic Institute and State University (VPI&SU) in December 1976. The degree of Master of Science in Chemical Engineering was awarded in August of 1979. Following three years of employment as a chemical engineer with the Naval Surface Weapons Center in Dahlgren, Virginia, he returned to VPI&SU to pursue the Doctor of Philosophy in Chemical Engineering. During his graduate career he was a Pratt Presidential Engineering Fellow for two years and was awarded the Cunningham Dissertation Year Fellowship for the final year of graduate study. He has coauthored 25 scientific papers concerning polymers and polymer composites, and is a member of the American Chemical Society, the American Institute of Chemical Engineers, the Society of Rheology, and the Society of Plastics Engineers. After receiving the Ph.D. he will join the Polymer Materials Science Group at Dow Chemical USA, Texas Operations in Freeport, Texas as a Senior Research Engineer. He is married to the former Martha Ann Hite of Christiansburg, Virginia.

A handwritten signature in black ink that reads "Martin R. Tant". The signature is written in a cursive style with a large, stylized 'M' and 'T'.