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INFLUENCE OF TRACE COMPONENTS ON THE VISCOELASTIC PROPERTIES OF A POLYMER SOLUTION

Seok H. Hong
Wendel J. Shuely

RESEARCH AND TECHNOLOGY DIRECTORATE

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Hong, Seok H., and Shuely, Wendel J.

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Research on characterization of viscoelastic properties of ultrahigh molecular weight polymer solutions led to the discovery of variations in rheological properties combined with variable dissolution behavior for certain polymer-liquid systems. The reference solutions exhibited extreme intra sample variations; therefore, the influence of processing and trace impurities on rheological property variance was studied. Measurements of first normal stress difference, apparent viscosity, and dynamic viscoelastic properties were performed as a function of controlled addition of components with specific molecular interactions with polymers or solvents (e.g., various salts, surfactant, and chelating reagents). In addition, processing treatments such as filtration and centrifugation were applied and their influence on rheological properties of the polymer solution was determined.

14. SUBJECT TERMS

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Additives	Apparent viscosity
Polymer solution	First normal stress difference

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PREFACE

The work described in this report was authorized under Project No. 1C161102A71A, Research in CW/CB Defense. This work was started in October 1986 and completed in February 1989.

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INFLUENCE OF TRACE COMPONENTS ON THE VISCOELASTIC PROPERTIES OF A POLYMER SOLUTION

1. INTRODUCTION

The viscoelastic properties of an ultrahigh molecular weight (MW) polymer solution varied during previous research involving dissolution and characterization of a proprietary polymer solution.[1] The polymer solution exhibited a decrease in viscosity as a function of storage period and temperature that might be explained in terms of kinetic dissolution processes. The polymer of interest is a copolymer of protic, hydrogen bond acceptor-donor repeat units such as aminoalkyl methacrylate and aprotic and dipolar repeat units such as alkyl methacrylate. The solvent system is a proprietary mixture of aliphatic alcohols and an aliphatic amine; therefore, complex hydrogen bonding interactions are possible between polymer and polymer as well as polymer and solvent.

A thorough study of the polymer solution over a period of 2 years led us to hypothesize that the fluctuation of viscoelastic properties of the polymer solution was not primarily due to any chemical change in the polymer system (e.g., polymer degradation, solvent-polymer reaction, or solvent reaction).[1,2,3] However, the polymer solution exhibited a decrease in viscosity as a function of time (months) and storage temperature. This large variation in viscosity as a function of time and temperature might be explained by kinetic variability of the dissolution process. In other words, the polymer-solvent system could be thermodynamically favored and stable; however, the rate of attainment of the equilibrium dissolution state can be extremely long and variable. Furthermore, ultrahigh MW copolymers, especially with considerable blocking, can form supramolecular structures of entangled coil doublets, triplets, and multiplets.[4] The dissolution kinetics for disentanglement of a multiplet supramolecular structure to an equilibrium network configuration might be quite slow for various reasons.[5] Two examples of these reasons are the small difference in the initial and final states and the mechanical inhibition of translational and segmental motions in such entangled systems.

This study is an experimental survey on influence of a wide variety of chemical functionalities on rheological properties of the polymer solution. Thus, a sample of the ultrahigh MW polymer solution was treated with various additives. These additives are both inorganic and organic salts, organic acids that include diacids, and a polymeric acid (i.e., a copolymer of alkyl methacrylate and methacrylic acid). This investigation also includes the effect of trace impurities typically found in polymers or solvents such as stabilizers and surfactants. From a technological perspective, the objective was to determine if these additives might be associated with undesirable viscosity fluctuations as a function of time. However, the related rheological measurements with a polymeric acid additive were directed toward exploiting the possibility of increasing polymer-polymer contacts and enhancing viscoelasticity. Also underway is the study of direct spectroscopic measurement of interaction between the polymer and the additive or solvents.[3]

2. REVIEW OF PHYSICAL INTERACTIONS

The polymers of interest generally contain a protic or basic monomer copolymerized with an aprotic dipolar monomer. The solvent system is a mixture of alcohols and a primary amine and, therefore, is entirely protic. In addition, certain control and/or comparative experiments were performed with low polarity or aprotic tertiary amine solvents.

Polymer-polymer hydrogen bonding interactions that should occur are between the proton of the secondary amine in aminoalkyl methacrylate donated to the corresponding acceptor nitrogen and/or carbonyl oxygen. These hydrogen bonds can be adjacent, intersegment, intrachain, and/or interchain. The cosolvents are protic donor-acceptors and, therefore, can form hydrogen bonds with the polymer donor-acceptors functionalities and among the other cosolvent components. The cosolvent system would be characterized as a nonaqueous solvent containing 0.2-0.4 wt% water with a dielectric constant between 4 and 5.

Published experimentation with dilute polyelectrolyte solutions comparing salt-free, ion-free, and counter-ion/salt containing solvents have shown the extreme difficulty in actually obtaining salt-free, ion-free solvents. Therefore, the alcohol-amine solvent mixture, like most industrial solvents, undoubtedly contains trace ionic and salt species. The following are examples of trace impurities that could interact with the copolymer by hydrogen bonding or complex formation to influence solubility and viscosity:

- Non-ionic surfactant (aromatic polyether from emulsion polymerization of the copolymer)

- Cellulosic fibers (from the filtration procedure after polymerization)

Possible trace impurities that could convert the neutral, weak polybase (copolymer) to a charged macro-ion include the following:

- Ion salts from steel container material
- Ions from glass containers
- Ionic surfactants
- Ionized water (pH effect)

By increasing the content of monovalent ions that convert the neutral polybase to a charged polymer would increase the dilute solution viscosity; the effect in the semi-dilute and concentrated regimes is potentially more complex. Divalent ions have the additional potential for creating crosslinks that lead to gel structures. Neutral salt impurities should solvate any polyionic site and reduce the dilute regime viscosity and, most likely, the moderate concentration regime viscosity.

The solution of alcohols, amines, and amino side-groups of the copolymer can be examined for structure formation based on an imbalance in relative hydrogen bond strengths that would favor a nonstatistical distribution of hydrogen bonding or proton transfer. The relative basicities of the primary amine versus the secondary or tertiary aminoethyl ester polymer side-groups will depend on solvent medium. For a nonaqueous solvent medium, the following orders of increasing basicity have been reported as a function of dielectric constant:[6]

Benzene (dielectric = 2.2): Sec>Tert>Prim

Dibutyl ether (dielectric = 3.1): Sec>Prim>Tert

Chlorobenzene (dielectric = 5.6): Tert>Sec>Prim

The alcohol-amine solvent mix has a dielectric constant of 4-5, which is similar to the chlorobenzene. On this basis, the primary amine would exhibit proton transfer preferentially to the secondary and tertiary aminoethyl polymer groups. The excess molar ratio of primary amine to polymer-bound secondary or tertiary amines argues against charge formation on the polymer. However, the relative basicities may be different in a dielectric medium of 4-5 that is protic. It should also be noted that relative proton-sharing strength in hydrogen bonding does not follow proton transfer strength. Overall and without specific experimental evidence to the contrary, one would have to assume a typical statistical fluctuation of transient hydrogen bonds rather than preferential structure formation.

2.1 Kinetics of Solvation of Megadalton Polymers and Influence on Polymer Solution Mixing Technology.

A polymer-solvent system might be thermodynamically favored and stable; however, the rate of attainment of equilibrium dissolution state can be extremely long. As the MW increases, supramolecular structures of entangled coil doublets, triplets, etc., persist to produce a quasi-distribution shifted to a higher MW. The supramolecular structures function similar to an increase in concentration of a high MW fraction and provide increased viscosities. The lifetime of these supramolecular structures is unknown, and the persistence of their viscous effects is a complex function of all parameters that influence kinetic processes (i.e., temperature and mechanical history, etc.). As the polymer concentration and resultant coil density increase, the degree of entanglement at equilibrium increases. The polymer concentration (8 g/dL) and MW [2-3 megadalton (Mamu)] or the limiting viscosity number (LVN) concentration product of about 24 indicate that the polymer/solvent mix lies beyond the transient entangled regime and in transition to the network-entangled regime (LVN times the concentration >20-30).[7]

The dissolution kinetics for disentanglement of a supramolecular structure to an equilibrium network configuration might be quite slow due to the small difference in the initial and final states and to the mechanical inhibition of translational and segmental motions in a network-entangled system.

The technological aspects of mixing megadalton polymer solutions are not well documented. The Federal Aviation Administration/Imperial Chemical Industries (ICI) Anti-Misting Fuel Program and Department of the Army (DA) dissemination programs are possibly the best sources of information on the state of this technology. The ICI Anti-Misting Polymer FM9 had to be formulated as a pre-swollen slurry to attain suitable mixing behavior. The DA programs have not yet solved polymer solvation preparation problems for relatively straightforward aprotic dipolar polymer/solvent pairs. For example, the U.S. Army Dugway Proving Ground (DPG) (Dugway, UT) has mixed K125/HD to a monitored viscosity for the last several years because of the inability to attain a reproducible viscosity with a specific polymer concentration (P. Harvey, DPG, UT, personal communication, 1985). To support this, a specific study was conducted at the Research Directorate, U.S. Army Chemical Research, Development and Engineering Center,* to define suitable pretreatment and mixing conditions for methacrylate terpolymer Acryloid K125 in diethyl malonate (DEM). Solutions of high MW poly(methyl methacrylate) homopolymer in DEM showed an erratic decrease in the viscosity between the preparation and the use in field trials. Each polymer MW in all these cases was above 2 Mamu. Specific technology is under development in the industry to address this problem area; high-volume, cryogenic polymer dissolution processes have been patented and scale-up is underway.[8] High volume, freeze-dried processing is a related candidate technology.

2.2 Preferential Solvation.

Preferential solvation phenomena can influence rheological behavior of copolymer/cosolvent systems.[9] The determination of the solubility of each homopolymer in each component of a cosolvent mixture would aid in determining the existence of preferential solvation and the clustering of specific solvent molecules at specific comonomer sites. The interaction of individual cosolvent-comonomer pairs is also important because of the composition heterogeneity in copolymers with substantially different reactivity ratios; such copolymers contain a distribution of copolymer ratios. Although the average ratio of comonomers might be 25:75 mole %, polymers of near 100% of each component might exist at the extreme tails of the composition distribution. Furthermore, considerable blocking of one monomer can take place, even with continuous feed, starved emulsion polymerization.[10] For these chains, long sequences of a single monomer block yield a polymer-solvent environment similar to the homopolymer.

The most extreme rheological behavior might be obtained when a homopolymer composition is insoluble in the cosolvent mixture and the composition distribution or blocking sequences produce some near homopolymer

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*Now known as the U.S. Army Edgewood Research, Development and Engineering Center.

chains. These insoluble-collapsed coils might be network-entangled with soluble copolymers. The equilibrium state for this small (near) homopolymer fraction would be precipitation from solution. The kinetics of precipitation through an entangled network might be responsible for viscosity fluctuations.

Very little published data exists on the viscosity behavior or rheological properties of preferentially solvated polymer solutions. A published account exists of the disparity between radius of gyration estimates by light scattering and viscometric techniques.[12] Recent rheological research has shown the enhanced normal stress and viscosity for solvents and the viscosity for solvents preferentially solvated at one comonomer(s) and insoluble in another, which are relative to other solvents with an equivalent LVN.[11] The anomalous rheological behavior might be obtained when the homopolymer of one comonomer is insoluble in the cosolvent mixture and the composition distribution or blocking sequences produce portions of copolymers with significant length resemble homopolymer. Therefore, diagnostic experiments for preferential solvation would be solubility and/or LVN determinations of homopolymers of each copolymer component in each solvent component.[12]

3. EXPERIMENTATION

3.1 Procedures.

The rheological properties were measured by employing a Rheometrics Fluid Rheometer, Model RFR 7800 (Rheometrics, Incorporated, Piscataway, NJ), with cone and plate fixture. The rheological properties of the reference solution were measured by four repetitions, and a 95% confidence interval was established. After additives were introduced into the solutions, each solution was tumbled by a 3-dimensional motion Turbula Mixer, Model T2C (Glenn Mills, Incorporated, Maywood, NJ), for at least 3 days to ensure complete mixing. The filtration was carried out utilizing sintered glass filters, medium and coarse, fitted into a 50-mL centrifuge tube (Konte Glassware Company, Vineland, NJ). The confirmation of the existence of such aromatic compounds as benzoic acid and 2,6-naphthalene dicarboxylic acid in the solution was performed using a Hewlett-Packard (Avondale, PA) Model 8452A Diode Array Spectrophotometer.

3.2 Materials.

The acid additives were obtained from ChemService, Incorporated (Media, PA), chemical kit and used without further purification. Ultrahigh MW methacrylate copolymer and methacrylic acid copolymer were obtained from PolyScience, Incorporated (Warrington, PA) and Rohm and Haas Company (Philadelphia, PA), respectively. The reference solutions were made from a stock solution of the copolymer in alcohols/amine (8 g/dL), which was prepared and equilibrated over 18 months. On completion of the dilution, the reference solution was divided into small samples. An appropriate amount of the additive was introduced to each sample. After adding the additives, each sample was tumbled on a 3-dimensional motion Turbula Mixer for at least 3 days to ensure complete mixing. Except for the case of the polymeric acid, the acidic additives were introduced so that their concentration was roughly an equal molar ratio to the concentration of amino units of the copolymer in the solution. The selection of the acids was based on the number of equivalents per molecule and the size.

4. RESULTS AND DISCUSSION

4.1 Filtration and Centrifugation.

The results of the measurement of rheological properties are summarized in Table 1. Filtration through a medium-sintered, glass filter showed anomalous behavior (Figure 1). However, the process of filtration took more than 2 hr, and the evaporation of the volatile solvent component might have occurred, changed the ratio of solvents, and increased the polymer concentration. Filtration through a coarse-sintered, glass filter required <30 min and did not affect the rheological properties of the polymer solution. This is shown in Figure 2.

4.2 Salts.

The additives were introduced so that their content was approximately 1 w/w% of the total solution in each case or roughly 1:1 molar ratio between the additive and amino units in the copolymer. The actual ratios based on the polymer concentration are in Table 1.

4.2.1 Organic Salts.

Based on the statistics of the experimental data in Table 1 (95% confidence interval), one can conclude that there was no statistically significant influence of the added organic salts on the rheological properties of the polymer solution. From the lowest molecular volume salt (MeNH3Cl) to the highest molecular volume salt [$(n\text{-Bu})_4NI$], the rheological properties of the polymer solution remained the same (Figure 3). Changing the cationic portion of the additive from a primary to a tertiary ammonium group neither causes a statistically significant difference nor changes the anionic portion of the additive (Figures 4 and 5).

4.2.2 Inorganic Salts.

The only soluble inorganic salts among the salts that were tested were KOH, LiBr, and LiCl. Adding these salts resulted in an increase in the first normal stress difference (FNSD), as well as an increase in the apparent viscosity (Table 1). The FNSD increased about 100%, whereas the apparent viscosity only increased about 30%. These values are shown in Figures 6 and 7. Generally, these salts in nonaqueous media tend to exist in clusters rather than as isolated ionic species. However, the structure of these clusters may render some partial charges on the surface. Therefore, there might be some dipolar interactions between the polymer chains [e.g., carbonyl groups and metallic end of the clusters (salts)]. These linkages can influence the formation of the supramolecular structures of the copolymers.

4.3 Organic Acids.

4.3.1 Monoacids.

The aliphatic acids introduced into the solution were in the liquid state. When these acids were added to the sample, a white cloud was formed at the drop site in the solution. However, after tumbling, the cloudiness disappeared and the solution retained its clear, yellow color. One possible explanation for this phenomenon is localized salt formation by the acid additive and the amine component, probably from the solvent rather than from the polymer; upon tumbling, this salt dissolved in the solvent to give a clear liquid (Table 2).

The rheological properties (especially FNSD) of the resulting solutions were quite different from those of the reference solution, which are shown in Table 2 and Figure 8. The size of the acids apparently did not influence the change in rheological properties. One of the possible explanations for the change in rheological properties is a somewhat weak hydrogen bond type interaction between the acid and the polymer chains, either in free-acid or clustered-salt form. One might expect a stronger influence by the diacids due to the fact that a diacid can form a bridge between polymer chains through both of the acidic functionalities.

The aromatic acid (benzoic acid), in its white crystalline form, was added. There was no apparent change when added, and the mixture remained unchanged (i.e., liquid phase and solid phase) after tumbling. Whether or not this solid phase was in the free acid form or in the salt form was not determined. The UV spectrophotometer of the separated liquid phase showed the presence of benzoic acid in the solution (Figure 9). However, the rheological properties of the separated liquid phase apparently showed no significant change (Figure 10). This might be due to the fact that there is not enough benzoic acid in the solution to influence the rheological properties of the solution. Although the solution is nominally saturated with benzoic acid, the ratio to protic aminoalkyl methacrylate functionality in the polymer should be well below equimolar.

4.3.2 Diacids.

As shown in Table 2, several diacids of different chain length were used, including aromatic acids (terephthalic acid and 2,6-naphthalene dicarboxylic acid). All the acids were in the solid state. The results were similar to that of benzoic acid (i.e., no apparent change in either the FNSD or the apparent viscosity) (Figure 11). This can also be explained in terms of low solubility and concentration of the acids in the polymer solution, which was in the case of the benzoic acid.

4.3.3 Polymeric Acid.

The polymeric acid used was a copolymer of the same alkyl methacrylate and methacrylic acid (9:1 molar ratio). The MW of this copolymer was around 1 Mamu. A solution of this polymer in alcohols/amine mixture, as well as a mixture of alcohols without amine, was prepared and mixed with appropriate ultrahigh MW copolymer solutions so that the ratio of the two polymeric species became 4:1, 6:1, and 8:1. Rheological properties and the calculated concentration of total polymers are in Table 3. As shown in Figure 12 and Table 3, the polymeric acid significantly altered the rheological properties, especially the FNSD.

4.4 Other Additives.

Some of the impurities typically found in monomers, polymers, and solvent systems that result from storing and/or processing were also studied. As shown in Table 4, the additives [2,5-di-t-butyl-hydroquinone, ethylenediaminetraacetic acid (EDTA), and surfactant] showed no influence on the rheological properties of the polymer solution.

5. CONCLUSION

Rheological properties of the filtered solutions (Figures 1 and 2) showed no apparent difference from those of the unfiltered reference solution (Figures 1 and 2). Also, rheological properties of the solutions with different organic salts showed no apparent difference from those of the reference solution. Solutions with inorganic salts (i.e., LiCl, LiBr, and KOH) showed an apparent increase in both apparent viscosity and first normal stress difference (FNSD). An example of a hypothesis for a mechanism for the change of rheological properties is the possibility of a weak cross-linking at carbonyl groups of the polymer. These salts are probably in the form of clustered, nondissociated species. The results suggest specific additional studies; nuclear magnetic resonance or other spectroscopic instrumentation would be the preferred technique for confirming the proposed cross-link structure, and further studies on acidic additives, as well as multivalent cationic salts additives, would be beneficial in establishing the possibility of cross-linking via weak intermolecular interactions between polymer coils.

An example of possible explanations of this change is a weak, hydrogen bond-type, bond formation at carbonyl groups of the polymer. The polymeric acid additive should enhance this effect since it can create multiple polymer-polymer contacts. Further studies with polymeric acid additives are in progress at the State University of New York at Stoneybrook (Stoneybrook, NY).

Rheological properties, especially FNSD, of the polymer solutions with monoacid additives exhibited significant increases from those of the reference solutions (Figure 9). Also, rheological properties of the solutions with polymeric acid showed significant differences from those of the reference solution (Figure 12). However, apparent viscosity of the aforementioned solutions showed less change when compared to the FNSD. Solutions with additives of low solubility showed no apparent difference in rheological properties from the reference solutions (Figures 10 and 11).

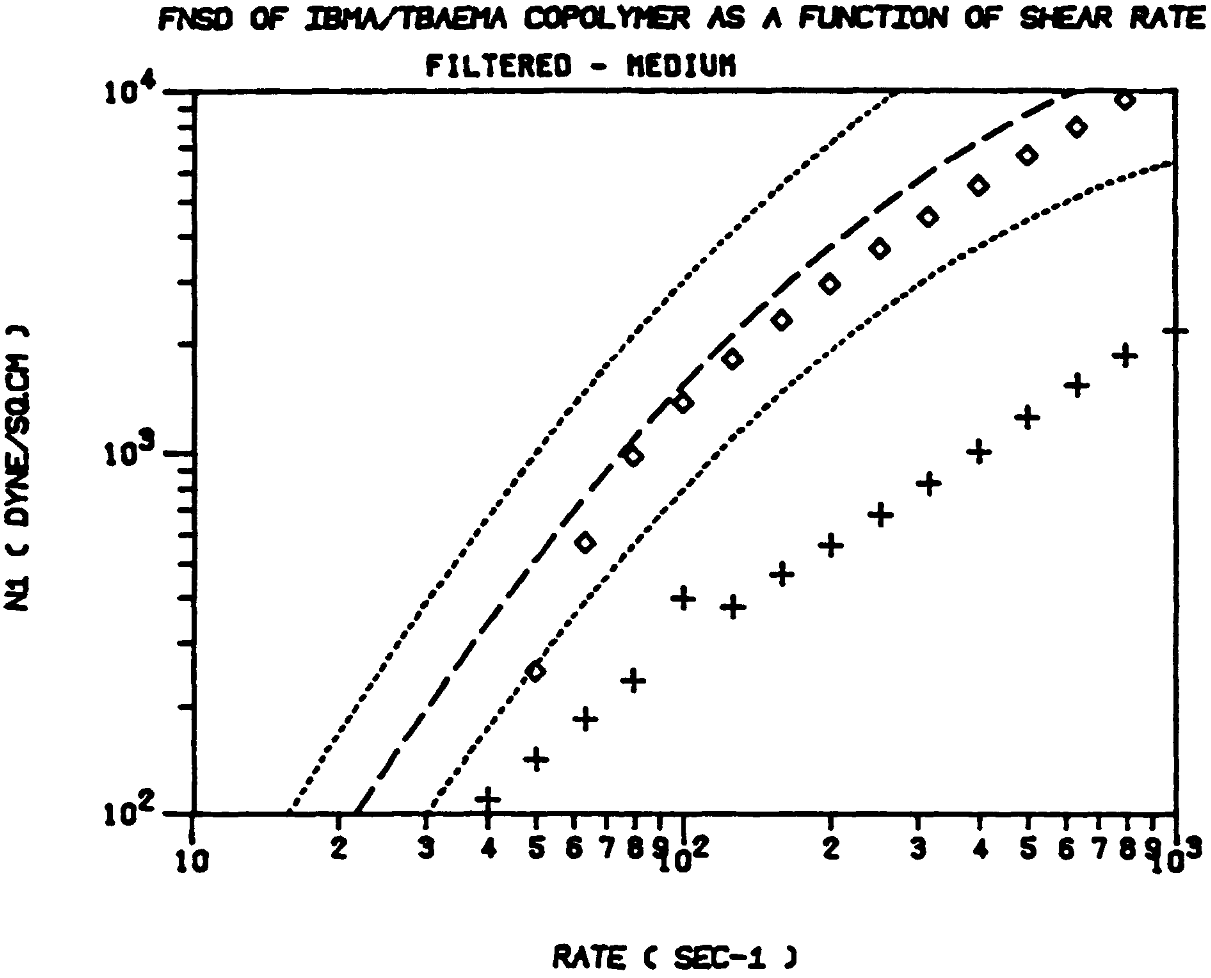

Figure 1. First Normal Stress Difference of Copolymer Solution After Filtration with Medium Filter Compared to that of Reference Solution

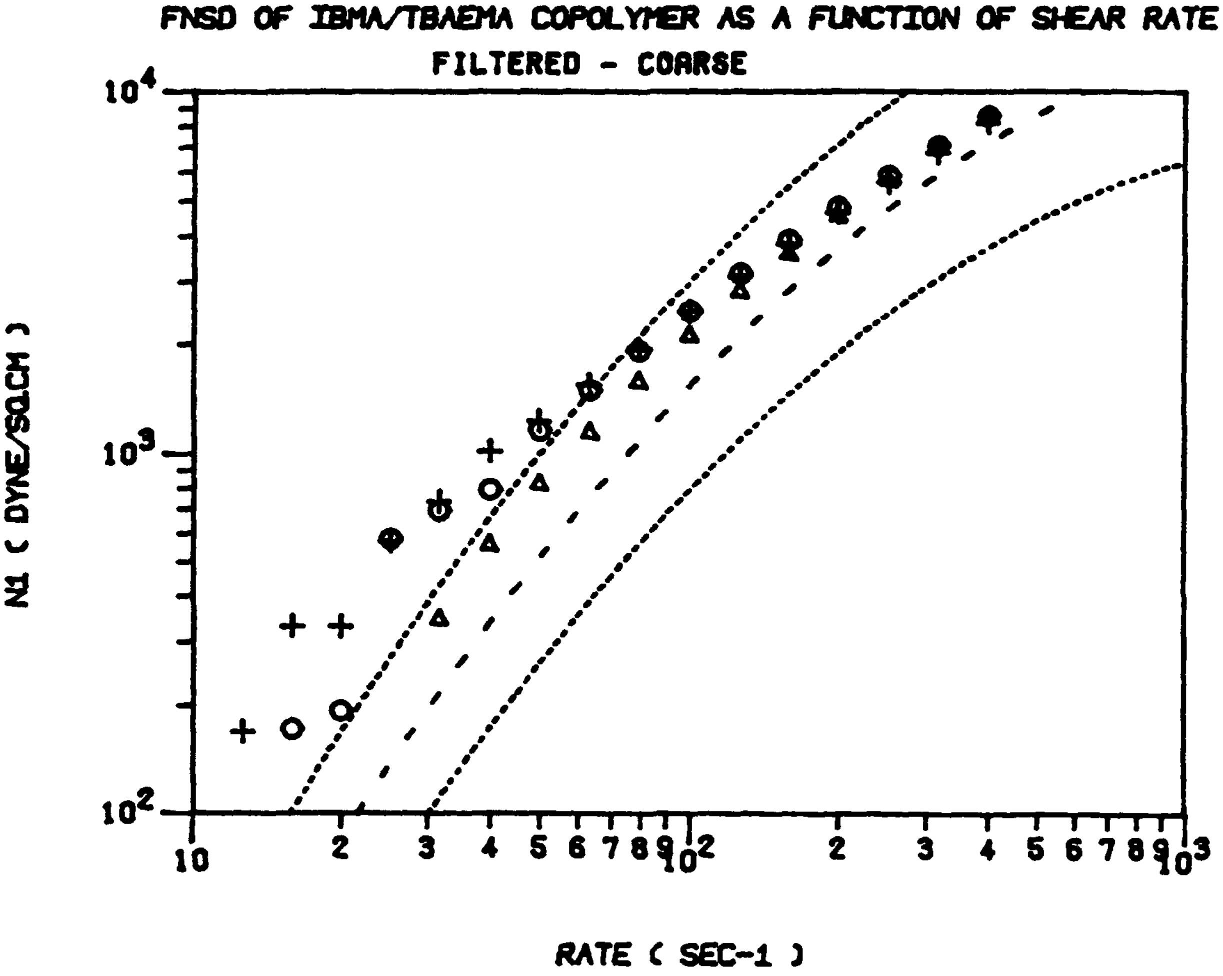

Figure 2. First Normal Stress Difference of Copolymer Solution After Filtration with Coarse Filter Compared to that of Reference Solution

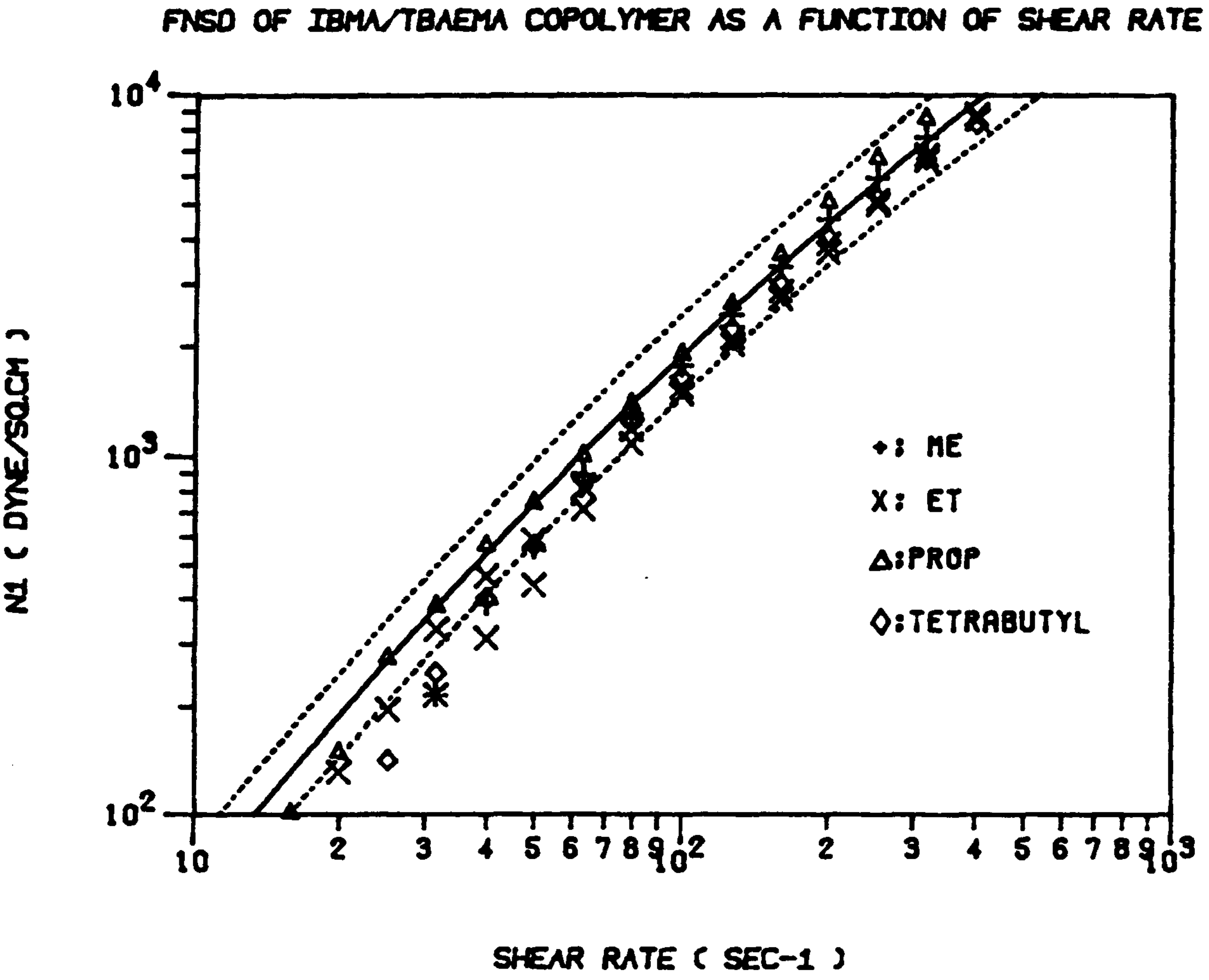

Figure 3. First Normal Stress Difference of Copolymer Solutions with Various Organic Salts Compared to that of Reference Solution

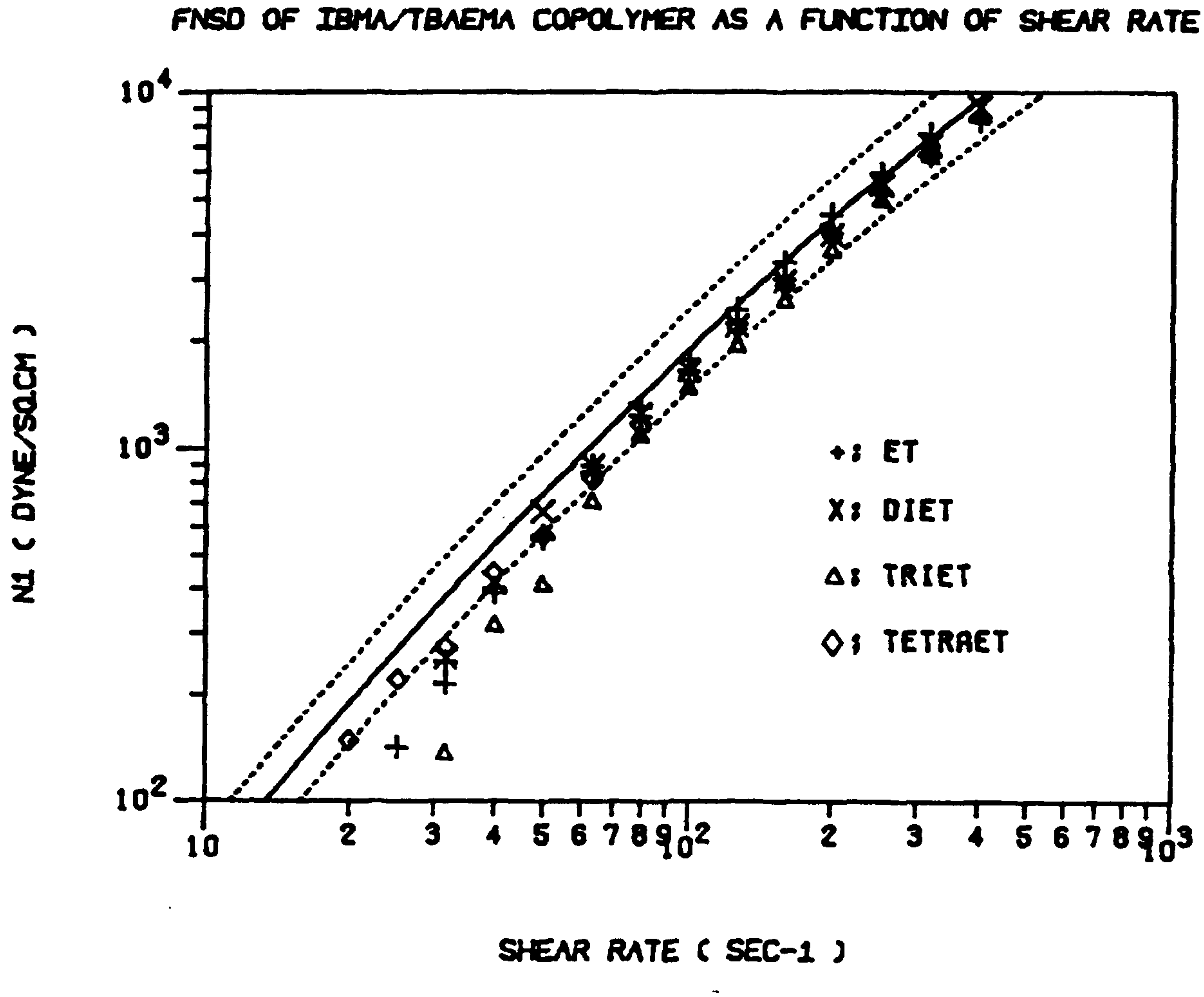

Figure 4. First Normal Stress Difference of Copolymer Solutions with Various Ethyl Ammonium Chlorides Compared to that of Reference Solution

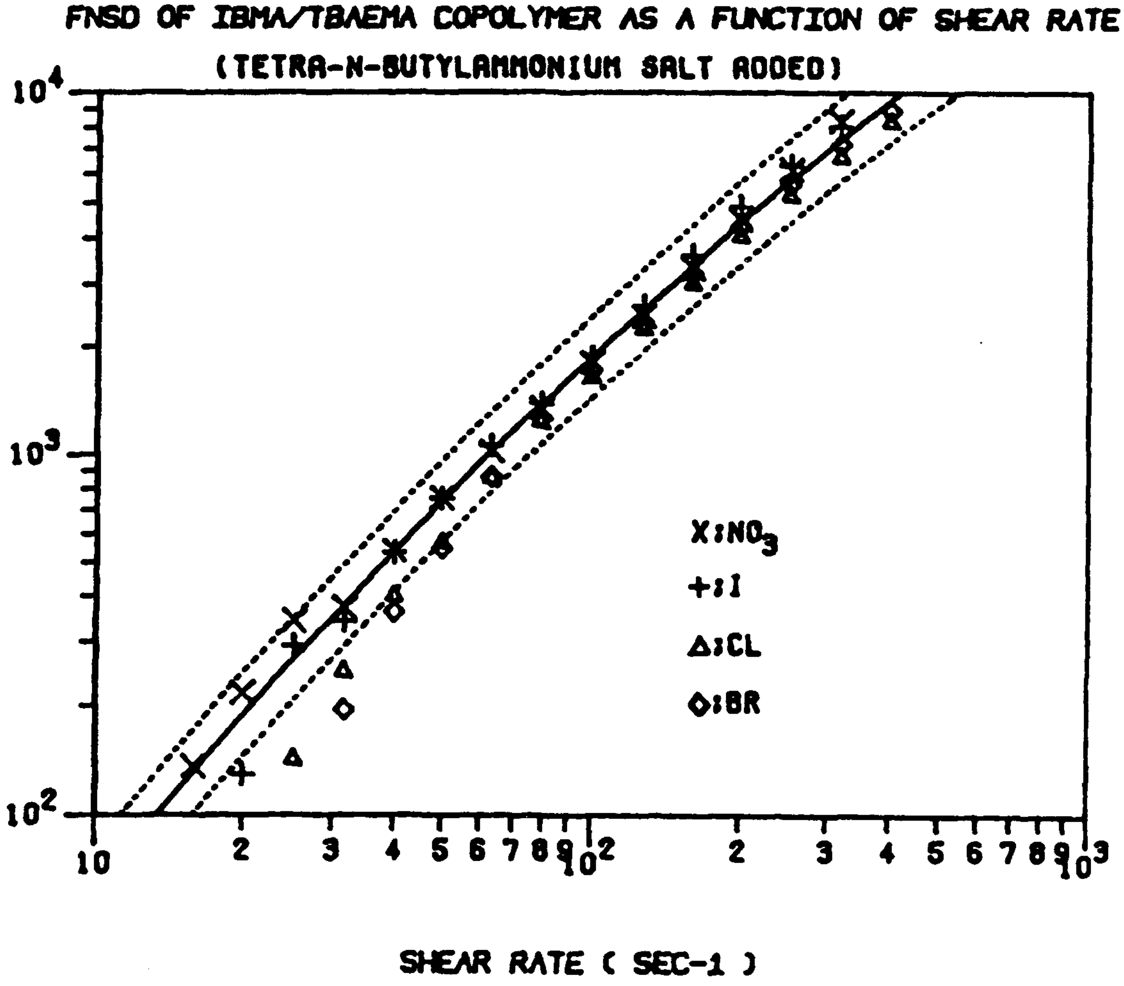

Figure 5. First Normal Stress Difference of Copolymer Solutions with Various Tetra-n-Butyl Ammonium Salts Compared to that of Reference Solution

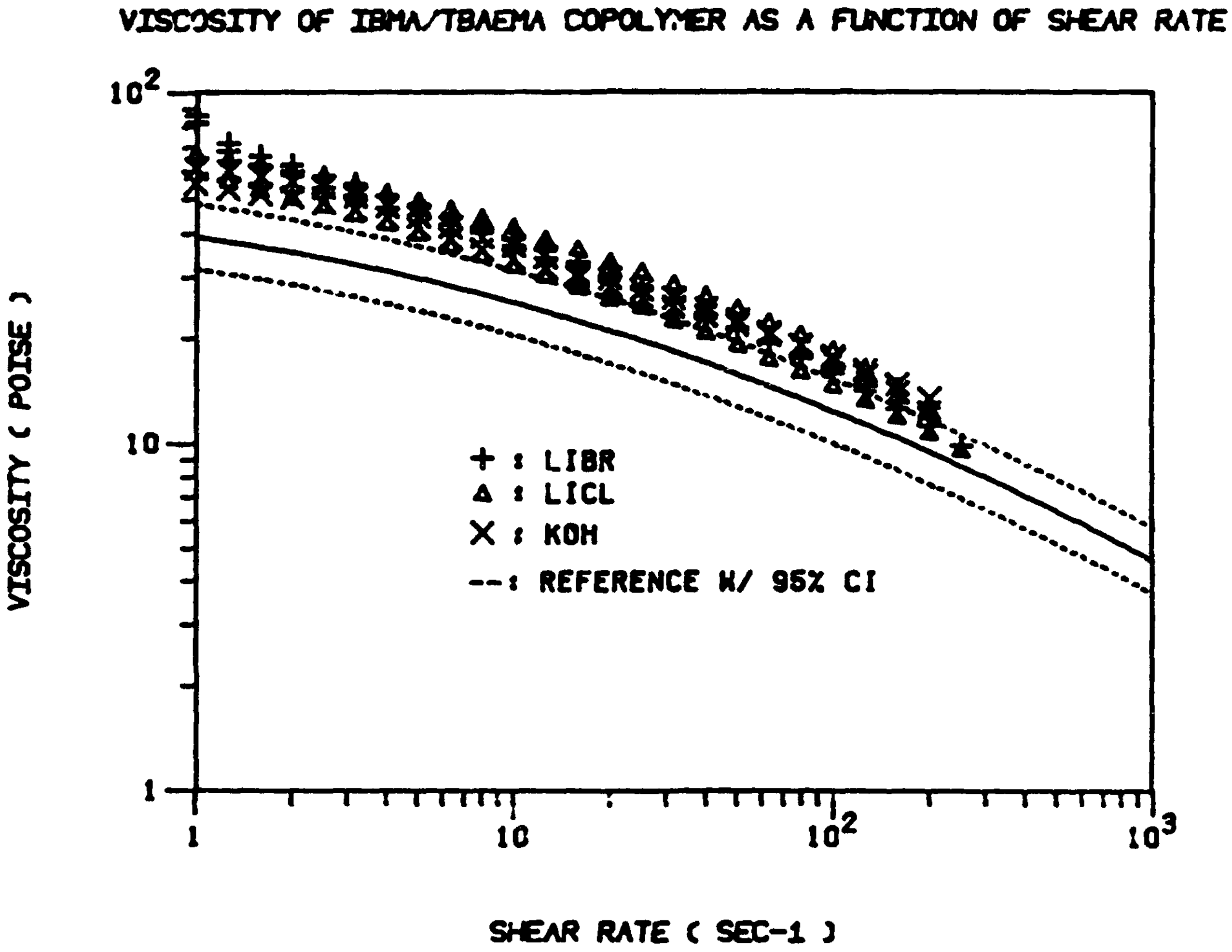

Figure 6. Apparent Viscosity of Copolymer Solutions with Various Inorganic Salts Compared to that of Reference Solution

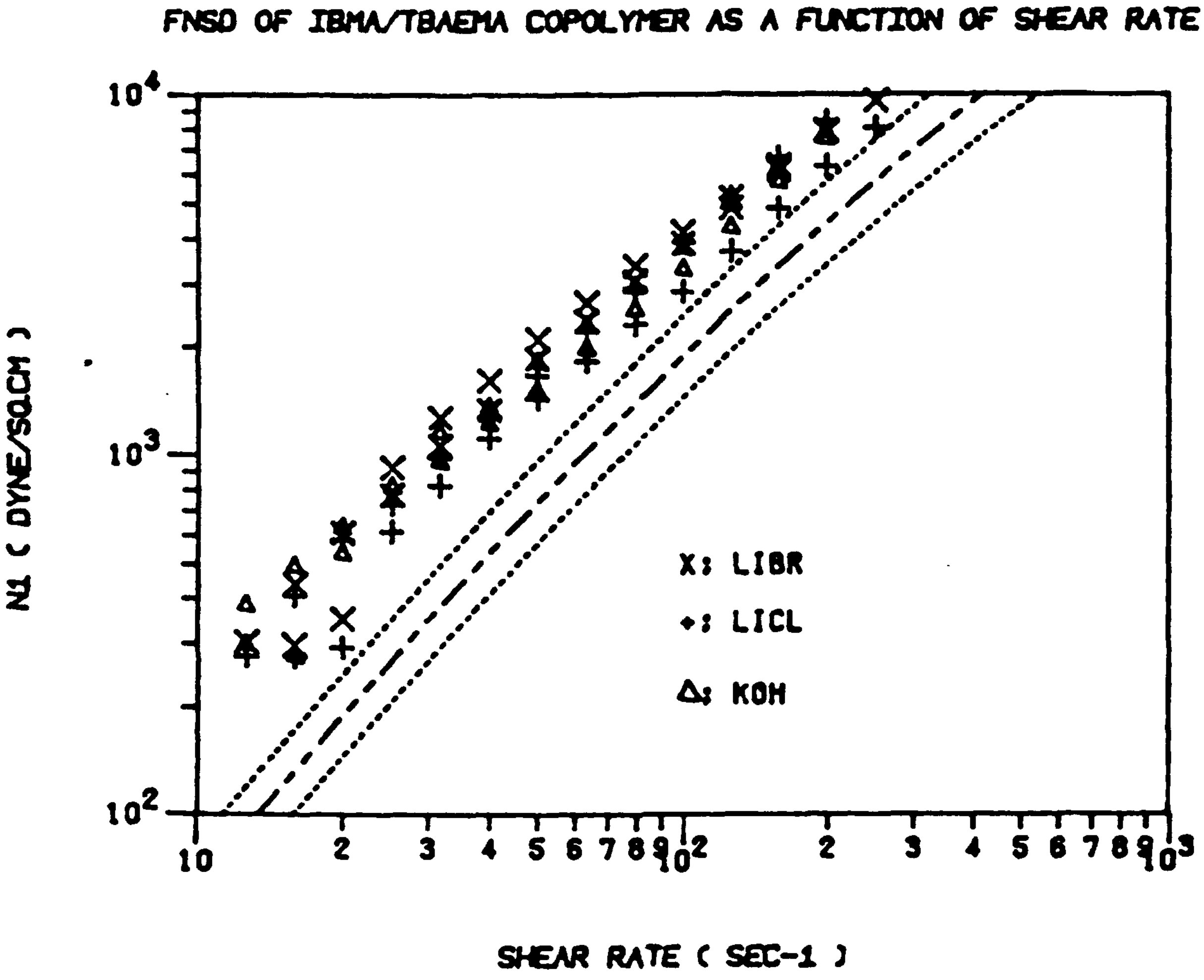

Figure 7. First Normal Stress Difference of Copolymer Solutions with Various Inorganic Salts Compared to that of Reference Solution

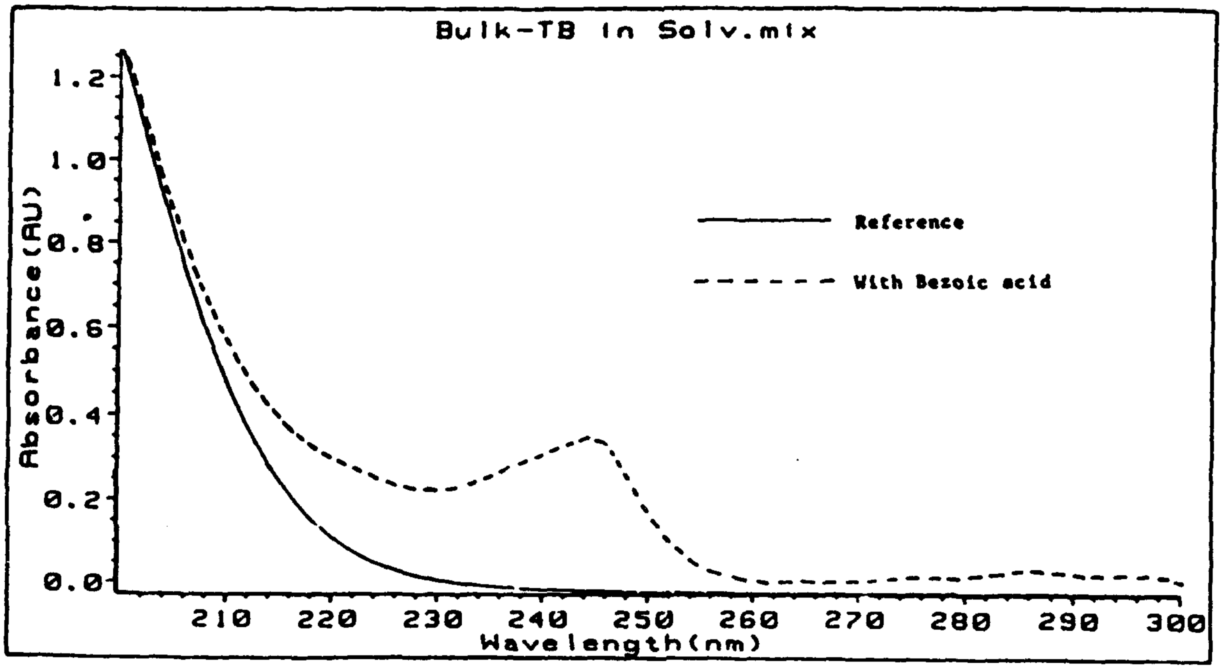

Figure 8. UV Spectra of Copolymer Solutions with and without Benzoic Acid

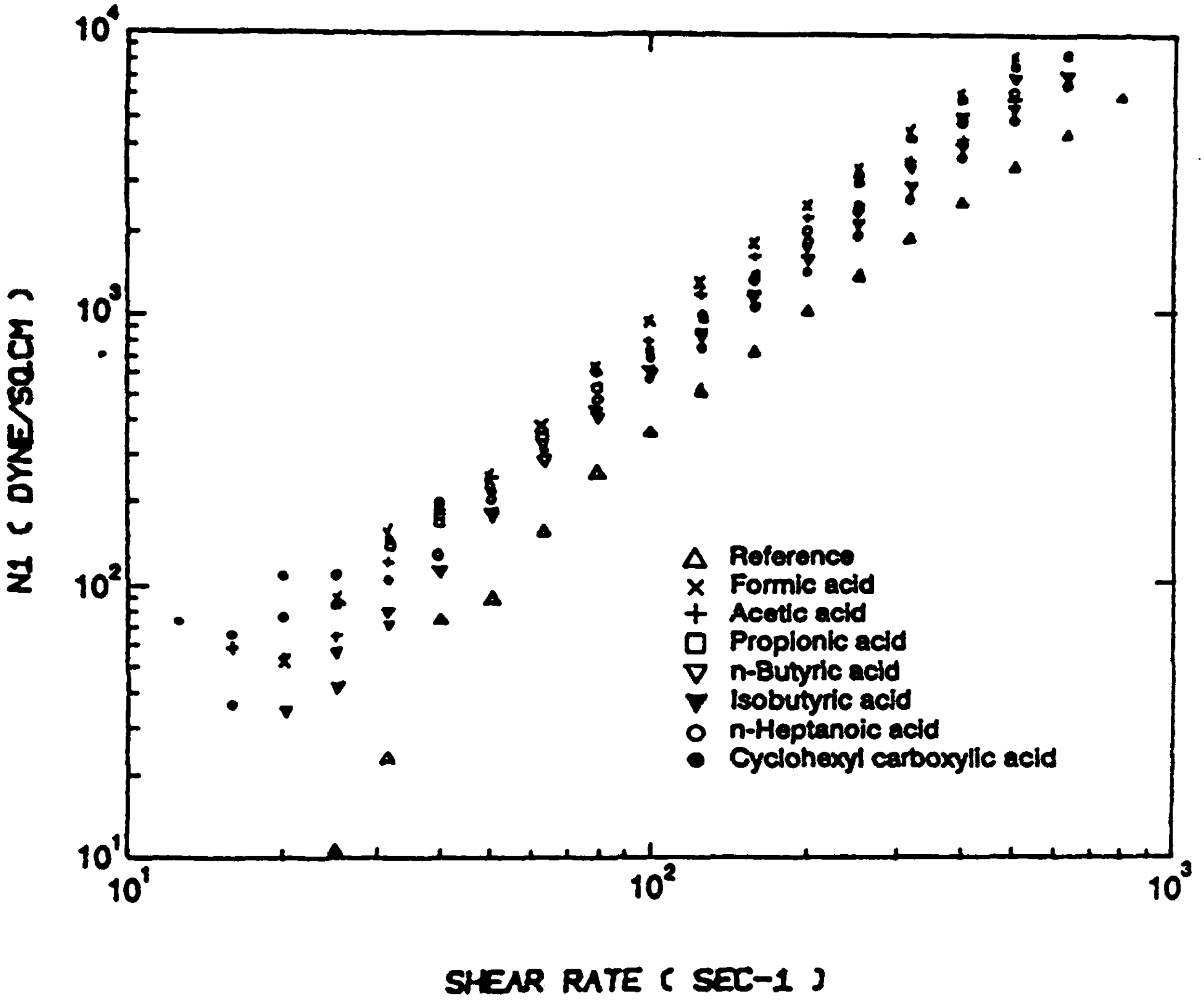

Figure 9. First Normal Stress Difference of Copolymer Solutions with Various Organic Monoacids Compared to that of Reference Solution

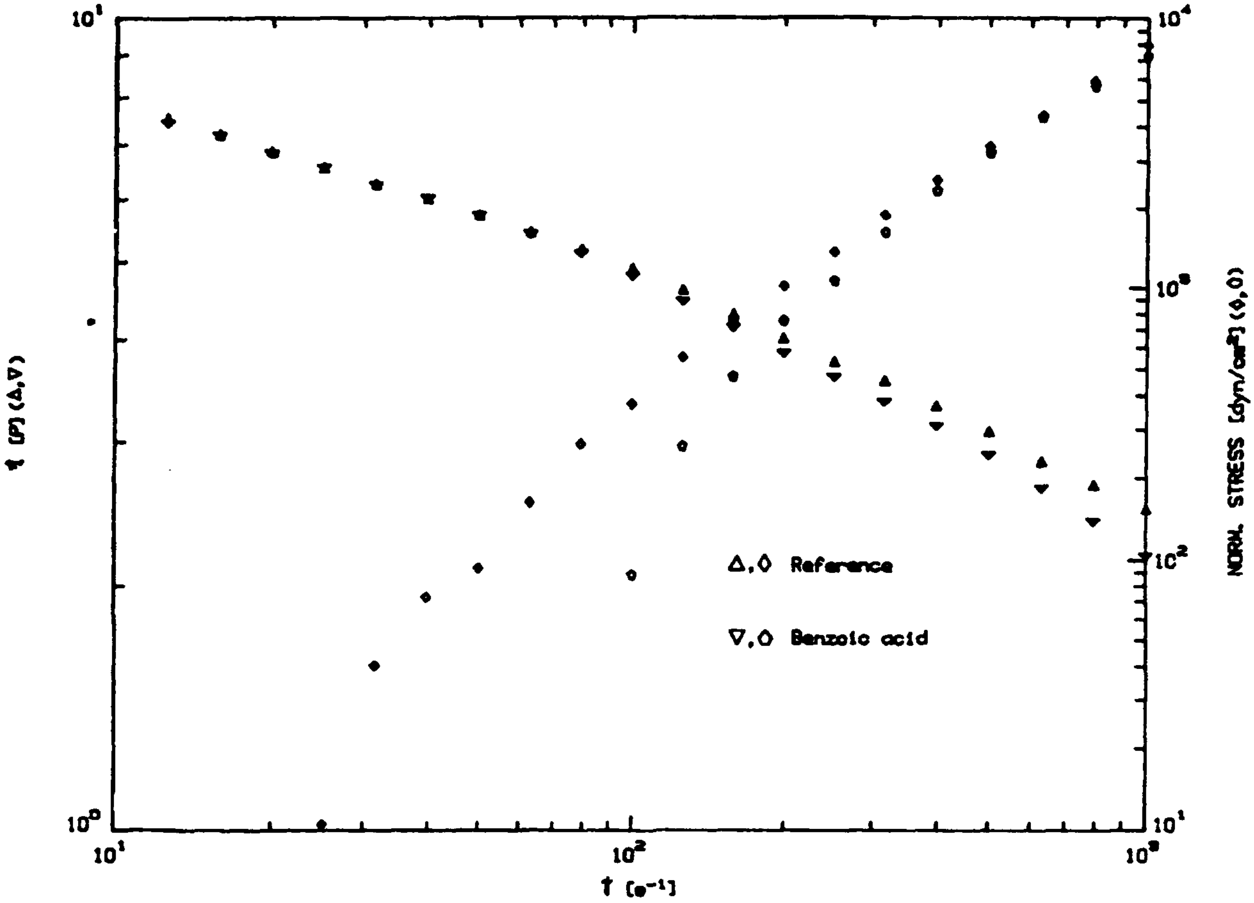

Figure 10. Viscoelastic Properties of Copolymer Solution with Benzoic Acid Compared to Those of Reference Solution

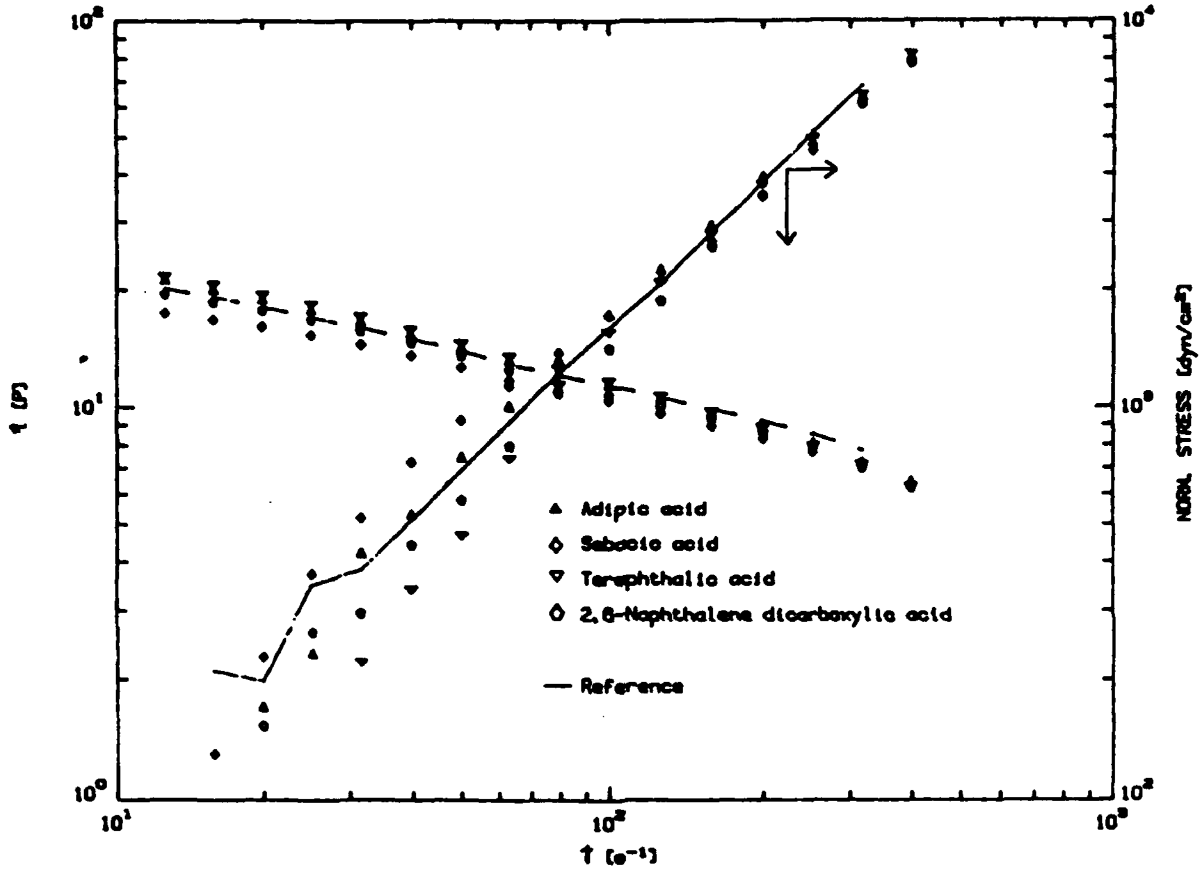

Figure 11. Viscoelastic Properties of Copolymer Solutions with Various Organic Diacids Acid Compared to Those of Reference Solution

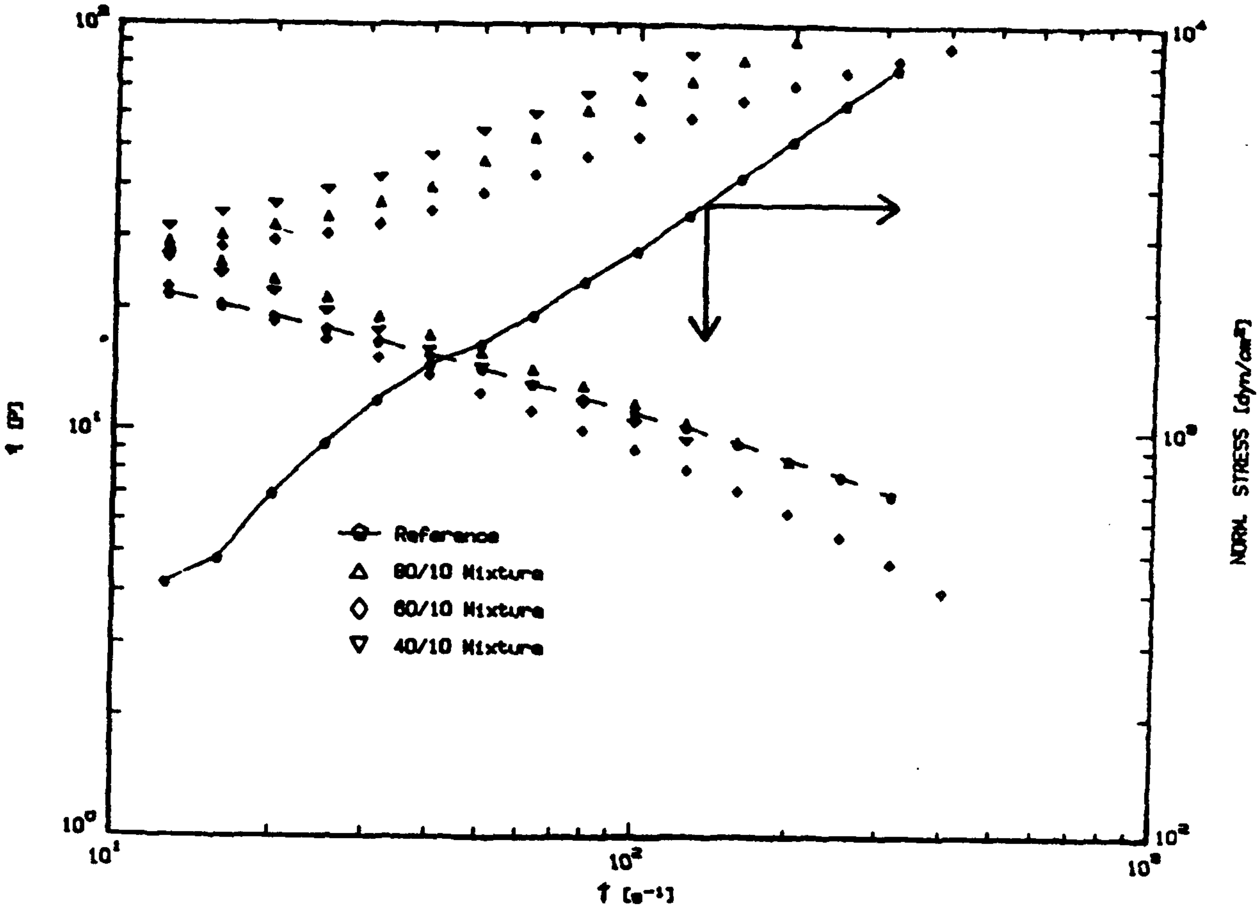

Figure 12. Viscoelastic Properties of Copolymer Solutions with Various Amounts of Polymeric Acid Compared to Those of Reference Solution

Table 1. Rheological Properties of the Copolymer/Solvent Mix with Various Additives

Additive	Wt. of Solution (g)	Wt. of Additive (g)	S[c]	% w/w	Molar Ratio[d]	AV[a] @12.6/s (cp)	FNSD[b] @100/s (d/cm^2)
Ref[e]						23.59	1857
						2.93	455
Lif	3.1048	0.0313	N	(1.01)	(2.7)	(23.7)	(1880)
LiC	3.0231	0.0313	Y	1.04	1.8	38.0[f]	3890[f]
						29.9[f]	2840[f]
LiB	3.2373	0.0314	Y	0.97	0.8	35.7[f]	4150[f]
						33.7[f]	3840[f]
LiO	3.2235	0.0324	N	(1.08)	(3.3)	N/D	N/D
NaF	3.0326	0.0287	N	(0.95)	(1.7)	N/D	N/D
NaC	2.6531	0.0275	N	(1.04)	(1.3)	N/D	N/D
NaBr	2.7747	0.0301	N	(1.08)	(0.8)	N/D	N/D
NaI	3.0523	0.0281	N	(0.92)	(0.5)	N/D	N/D
NaOH	3.4948	0.0397	N	(1.14)	(2.1)	N/D	N/D
KF	3.2243	0.0291	N	(0.90)	(1.2)	(23.9)	(1800)
KCl	3.0758	0.0323	N	(1.05)	(1.0)	(21.9)	(1500)
KBr	3.0026	0.0313	N	(1.04)	(0.7)	(25.4)	(2080)
KI	3.0665	0.0328	N	(1.07)	(0.5)	(28.1)	(2490)
KOH	3.6046	0.0380	Y	1.05	1.4	31.7[f]	3250[f]
						34.0[f]	3740[f]
CsF	3.2859	0.0307	N	(0.93)	(0.5)	N/D	N/D
CsCl	2.9119	0.0294	N	(1.01)	(0.5)	N/D	N/D

Table 1. Rheological Properties of the Copolymer/Solvent Mix with Various Additives (Continued)

Additive	Wt. of Solution (g)	Wt. of Additive (g)	S[c]	% w/w	Molar Ratio[d]	AV[a] @12.6/s (cp)	FNSD[b] @100/s (d/cm^2)
Ref[e]						23.59	1857
						2.93	455
CsI	3.0603	0.0330	N	(1.08)	(0.3)	N/D	N/D
$MeNH_3Cl$	3.4970	0.0401	Y	1.15	1.3	22.2[f]	1770[f]
						35.2[f]	4010[f]
$EtNH_3Cl$	3.8852	0.0420	Y	1.08	1.0	21.3[f]	1530[f]
						22.6[f]	1470[f]
$PrNH_3Cl$	3.4144	0.0402	Y	1.18	0.9	23.3	1910
Et_2NH_2Cl	3.7793	0.0398	Y	1.05	0.7	22.7	1640
Et_2NHCl	3.6362	0.0410	Y	1.13	0.6	20.5	1460
Et_3NCl	3.7481	0.0406	Y	1.08	0.5	20.1	1570
Bu_4NCl	3.0489	0.0281	Y	0.92	0.3	22.9	1630
Bu_4NBr	2.7251	0.0316	Y	1.16	0.3	23.4	1720
Bu_4NI	3.3966	0.0309	Y	0.91	0.2	24.8	1910
Bu_4NNO	2.7701	0.0291	Y	1.05	0.3	22.4	1810

a. Apparent Viscosity
b. First Normal Stress Difference
c. Solubility:
    Y - Solution was homogeneous
    N - Solution still had solid phase (additive) in it after 7 days of mixing
d. Molar ratio of the additive to the amino group content (normalized) of the copolymer in the solution
e. Average of 4 measurements
f. Duplicate measurements

Table 2. Selected Rheological Properties of the Methacrylate Copolymer Solution with Acidic Additives

Additive	% w/w of Additive	Molar Ratio[a]	Sol[b]	Apparent Viscosity @20/s (poise)	FNSD[c] @100/s (dyne/cm)
<u>Monoacid</u>					
Reference				6.83	372
				7.03	353
				7.16	392
Formic acid	5.59	1.13	S	7.26	928
Acetic acid	6.35	1.00	S	7.76	782
Propionic acid	7.65	1.01	S	7.38	673
n-Butyric acid	8.86	1.01	S	7.00	595
Isobutyric acid	9.08	1.02	S	7.45	678
n-Heptanoic acid	12.65	1.02	S	7.68	685
Cyclohexane carboxylic acid	12.06	1.00	S	7.03	564
Benzoic acid	nd	nd	I	7.16	262

Table 2. Selected Rheological Properties of the Methacrylate Copolymer Solution with Acidic Additives (Continued)

Additive	% w/w of Additive	Molar Ratio[a]	Sol[b]	Apparent Viscosity @20/s (poise)	FNSD[c] @100/s (dyne/cm)
<u>Diacid</u>					
Reference				18.1	1590
Adipic acid	2.02	1.2	I	18.7	1710
Sebacic acid	1.59	0.7	I	16.0	1700
Terephthalic acid	1.71	0.9	I	19.5	1560
2,6-Naphthalene dicarboxylic acid	2.36	0.9	I	17.8	1420

a. Molar ratio of the equivalent in the additive to the amino group content (normalized) of the copolymer in the solution

b. Solubility - S means the solution was homogeneous and I means the solution still had solid phase after tumbling at least 3 days.

c. First Normal Stress Difference

Table 3. Selected Rheological Properties of the Methacrylate Copolymer in Alcohol Mixture with Polymeric Acid Additive

Solution*	Total Polymer Concentration (g/dL)	Apparent Viscosity @100/s (poise)	FNSD @100/s (dyne/cm^2)	Ratio to Reference
Reference	4	11.1	2800	1
80/10 Mixture	3	11.5	6500	2.3
60/10 Mixture	2.8	8.9	5290	1.9
40/10 Mixture	2.5	10.5	7530	2.7

*Ratios shown are Methacrylate copolymer/polymeric acid

Table 4. Rheological Properties of the Copolymer/Solvent Mix with Various Additives

Additive	Wt. of Solution (g)	Wt. of Additive (g)	S[c]	% w/w	Molar Ratio[d]	AV[a] @12.6/s (cp)	FNSD[b] @100/s (d/cm^2)
Ref[e]						23.59	1857
						2.93	455
EDTA	2.9268	0.0308	N	1.05	0.3	26.6	2260
HQ[f]	3.4359	0.0317	Y	0.92	0.3	25.2	2020
Surf[g]	4.0211	0.0382	N	(0.95)	-	25.6	1990

a. Apparent Viscosity
b. First Normal Stress Difference
c. Solubility:
  Y - Solution was homogeneous
  N - Solution still had solid phase (additive) in it after 7 days of mixing
d. Molar ratio of the additive to the amino group content (normalized) of the copolymer in the solution
e. Average of four measurements
f. 2,5-di-t-butylhydroquinone
g. Non-ionic surfactant

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