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A new NMR method for measuring the crystallization kinetics of polymers under high pressure, sensitive on a molecular scale to the dynamics of chain motion, was developed. The very rapid formation of extended chain crystals of polyethylene was directly observed. The technique has much promise for future experiments including polymer crystallization, melting and annealing. Polarization microscopy and NMR experiments on various alkali salts of alkalicarboxylates elucidated the dynamic structure of the smectic phase of

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these interesting ionic liquid crystalline materials. Experiments on highly viscous liquids explained the origin of the anomalous discontinuity observed in the temperature dependence of the shear viscosity of glass forming liquids. Molecular level interpretation of the coupling between translational and rotational motions in viscous liquids was achieved. The Debye and Stokes-Einstein equations were found to be applicable at the molecular level in viscous liquids. Volume effects were shown to be important for dynamics of viscous liquids. FINAL REPORT, NMR Study of Disordered Materials Under Extreme Conditions of Pressure and Temperature, AFOSR-81-0010.

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CONTENTS

Summary of Accomplishments

The main goal of the research supported by this grant has been the advancement of our fundamental understanding of the relationship between the atomic and molecular level properties and the macroscopic properties of the following classes of disordered materials: thermotropic ionic liquid crystals, supercooled highly viscous liquids, gels and polymers. An important part of our work was further development of unique NMR and laser scattering instrumentation to permit measurements of various disordered materials under extreme conditions of pressure and temperature.

In our polymer studies a new NMR method for measuring the crystallization kinetics of polymers under high pressure, sensitive on a molecular scale to the dynamics of chain motion, was developed. The very rapid formation of extended chain crystals of polyethylene was directly observed. The technique has much promise for future experiments including polymer crystallization, melting and annealing.

In the area of thermotropic ionic liquid crystals our polarization microscopy and NMR experiments on various alkali salts of alkalicarboxylates elucidated the dynamic structure of the smectic phase of these interesting ionic liquid crystalline materials.

The main general results of the experiments on highly viscous liquids can be summarized as follows: explanation of the origin of the anomalous discontinuity observed in the temperature dependence of the shear viscosity of glass forming liquids; molecular level interpretation of the coupling between translational and rotational motions in viscous liquids; applicability of the Debye and Stokes-Einstein equations at the molecular level in viscous liquids; importance of volume effects on the dynamics of viscous liquids.

Our systematic experiments to improve the microscopic understanding of the sol-gel process for preparing glasses and ceramics focused on the following problems. High resolution ^{29}Si NMR was employed at the molecular level to follow hydrolysis and condensation processes during the sol-gel process. For the first time, laser Raman scattering technique was used to follow the reaction kinetics leading to the SiO_2 networks of the wet gel. Using both NMR and Raman techniques the effect of high pressure on polymerization kinetics of the sol-gel process was investigated. It was shown that high pressures considerably enhance the reaction rate and reduce the gelation time without altering the condensation mechanism which operates during the initial stages of the polymerization process. The role of various chemical additives, including formamide was investigated by NMR, Raman and chemical techniques.

1. Comments on Unique Character of Our Research Effort

There are several specific aspects of our work which make our re-
search efforts unique. First, about 16 years ago we started our measure-
ments on liquids using pressure as an experimental variable because we
realized that only by separating the effects of density and temperature
on the molecular motions one can unravel the details of the dynamic
structure of liquids and other disorder materials. Therefore, we devel-
oped unique NMR instrumentation (1-5) which allowed us to carry out the
NMR experiments on various disordered systems over a wide range of pres-
sures and temperatures. There is currently no other laboratory in the
U.S.A. and abroad with comparable performance features of the experimen-
tal NMR high pressure setup. Second, our research group is the only one
which uses two powerful techniques - NMR and also laser Raman scattering
on a specific material (6-8). Clearly, this approach results in a sig-
nificant synergistic effect. In order to fully exploit the NMR or Raman
data our group also measures more mundane but necessary properties such
as PVT, diffusion and shear viscosities. Third, we have adopted a sys-
tematic approach in our studies, which approach is a prerequisite for
successful solution of the complex problem of liquids, gels, glasses and
polymers. Fourth, our experiments are always conceived with a specific
goal of either testing current theories or providing new results which
serve as a basis for developing new theoretical models.

2. Research Accomplishments Under Grant AFOSR 81-0010

2.1 Polymers

2.11 Entanglement and Elasticity in Polybutadiene Networks

Our previous studies of polybutadience melts and networks have
examined various phenomena at the molecular level by means of NMR relaxa-
tion measurements. Liu and Jonas (9) reported the pressure, temperature,
and frequency dependence of segmental motion and the glass transition in
cis-1,4-polybutadiene and other elastomers. Munie, Jonas, and Rowland
(10) analyzed segmental motion in peroxide crosslinked polybutadiene
networks as a function of crosslink density, temperature, and resonance
frequency. Munie (11) examined the relaxation of monodisperse poly-
butadiene melts as a function of temperature and pressure.

In the recent study (12) these techniques were combined with elas-
ticity measurements to examine the effect of entangled chains on both the
microscopic and the macroscopic scale. Our goal in this study was to
explore further the contributions of the entangled sol molecules and of
the trapped entanglements formed during network production. Peroxide
crosslinked networks were prepared from monodisperse polybutadienes of
two different molecular weights. Networks were crosslinked at high and
low dilution to vary the amount of chain entanglement. Each network was
then divided into two samples and the sol fraction was extracted from one
of these samples. The unextracted and the sol-extracted networks were
studied by NMR relaxation techniques as a function of temperature. The
elastic modulus was determined for all networks by stress relaxation
measurements.

By comparing stress relaxation data for both sol-containing and sol-extracted networks the effect of the entangled sol molecules on the elastic modulus were shown. NMR measurements were used to observe the effect of sol extraction on the network and to probe the effect of these entangled molecules over a broad frequency range. The elasticity results were examined together with the NMR results for evidence of trapped entanglements. The NMR results were also compared to previous studies involving damage healing and incomplete gel formation.

2.12 Kinetics of Crystallization of Polymers Under High Pressure

It should be emphasized that during the studies of polymers we developed a new NMR technique (13) for the study of crystallization of polymers under high pressure. We have successfully used the newly developed NMR technique for the study of kinetics of crystallization of polymers under high pressure on two systems: trans-polyisoprene and polyethylene. Data was obtained on the crystallization kinetics of trans-polyisoprene at 70°C at 1 kbar and 3 kbar. Polyethylene was studied at 117°C and atmospheric pressure and at four different temperatures each at pressures 1, 2, 3, and 4 kbar. Two additional measurements at 1 kbar were made to display the reproducibility of the measurement.

Kinetics data are often interpreted using the Avrami equation

$$1 - X(t) = e^{-kt^m}$$

where $X(t)$ is the degree of crystallinity. The coefficient m provides information on the nucleation process (heterogeneous in our case due to microscopic impurities) and on the growth geometry. There was a continuous change in m with increasing crystallinity. We observed an initial decrease followed by a continuous increase in the dimensionality of crystal growth. We also observed kinetic changes at high pressure which correspond to the change in crystal growth habit above 3 kbar. Much higher sensitivity to small changes in the process are possible because the measurement was performed in situ with continuous automated sampling.

In conclusion, we have developed a successful new method for measuring the crystallization kinetics of polymers under high pressure, sensitive on a molecular scale to the dynamics of chain motion. The very rapid formation of extended-chain crystals of polyethylene has been directly observed. A decrease in the surface energy of the crystal nucleus with pressure is indicated. The technique has much promise for future experiments including polymer crystallization, melting, and annealing.

2.2 Thermotropic Ionic Liquid Crystals

2.21 Introduction

The short-chain alkali metal alkyl carboxylates $C_nH_{2n + 1} COO^- NA^+$ with n < 7 form ionic mesophases (14) after melting of the solid and only at higher temperatures pass into a clear ionic melt. There has been considerable interest in NMR relaxation experiments to probe molecular motions in thermotropic and lyotropic liquid crystals. The molecular

length to width ratio of approximately 4 or larger is usually considered
to be of major importance in explaining the properties of these systems.
Some of the short chain carboxylates, however, form a group of compounds
exhibiting mesophases yet have a length to width ratio of less than 2.
The unusually small magnitude of this ratio along with the fact that very
few possible conformations of the ion exist make the properties of these
salts of interest as model compounds for complex liquid-crystalline
systems. The relative structural simplicity of these organic salts make
them excellent model systems which permit investigation of effects of
structural changes in closely related molecules. It appears quite prom-
ising that systematic studies will elucidate the role of harsh-short
range repulsive forces, and of long range electrostatic forces on forma-
tion of these ionic mesophases and their dynamic structure. Accompanying
investigations of the crystalline solid state focusing both on the solid-
solid transformations, the solid-mesophase transformation, and molecular
motions in the solid will help to understand better the structure of the
mesophases and also may contribute to our knowledge of melting disordered
organic solids.

These unusual mesophases are stable over a wide temperature range
(100°C) relative to normal liquid crystalline phases and have potential
technological application in areas of battery technology, high tempera-
ture thermography, and liquid crystalline conductive polymers and mem-
branes. It was therefore worthwhile to explore properties or factors
which promote ionic mesophase stabilization.

2.22 Recent Research Accomplishments

After initial NMR experiments (15,16), six major studies have been
finished:

1) Polarization microscopy (17) has been used to study the ionic meso-
   phases of melts of short chain sodium alkyl carboxylates. The smec-
   tic A or neat structure was confirmed for all the sodium carboxylates
   studied: isovalerate, n-butyrate, n-valerate, n-hexanoate and n-
   heptanoate. The domain sizes and transition temperatures were re-
   ported and an empirical correlation between birefringence and the
   order parameter was observed. The birefringence was predicted to be
   negative for all the compounds studied. It is interesting to note
   that sodium isovalerate exhibits quite different properties from
   those found for the other n-alkyl carboxylates. Both the birefrin-
   gence temperature coefficient and the average domain size (500 μm)
   are unusually large for sodium isovalerate.

2) The ^{1}H and ^{23}Na NMR studies (18) of smectic ionic mesophases of
   molten sodium n-butyrate and sodium isovalerate were reported over
   the temperature range of the stability of the liquid crystalline
   phases. The ^{1}H spin-lattice relaxation times, T_1 at v_o - 9.2, 24.3,
   and 60 MHz for the anions of both the systems were interpreted in
   terms of diffusion intermolecular relaxation mechanism. The pre-
   dicted anion diffusion coefficients are in agreement with those
   measured directly by spin-echo technique and indicate that the anion
   diffuses rapidly. In contrast to the T_1 relaxation mechanism the
   results obtained for the proton relaxation times in the rotating
   coordinate frame $T_{1\rho}$ indicate that the order-fluctuation relaxation

mechanism determined the frequency dispersion of $T_{1\rho}$. The analysis of the $T_{1\rho}$ data provides an approximate measure of the order parameter S as a function of temperature. Fourier transform spectra of the ^{23}Na transitions show that the electric field gradient (EFG) at the Na^+ ion is nonaveraged and of such a strength as to produce a second order quadrupole effect in the spectra of the central transition. From the first-order splitting, the quadrupole coupling constant (QCC) is obtained as a function of temperature. The gradual temperature change of QCC demonstrates that only a single liquid crystalline phase exists over the temperature interval of the stability of the smectic mesophase. Using approximate analysis the correlation time τ_c for the EFG fluctuation is obtained from the ^{23}Na T_1 data for the melts of both sodium n-butyrate and sodium isovalerate.

3) The ^{23}Na spin-lattice relaxation times, T_1, were reported for molten sodium n-alkyl carboxylates including n-valerate, n-hexanote, and n-heptanoate (19). The temperature range studied covered both the liquid crystalline smectic mesophase and the isotropic melt. The Fourier transform ^{23}Na NMR spectra of the mesophase show the presence of the second-order quadrupole shift in the ^{23}Na central transition in spite of the rapid Na^+ and carboxylate motion ($\omega_0\tau_c \ll 1$). This second-order quadrupole shift was observed earlier for sodium isovalerate and sodium n-butyrate. The ^{23}Na quadrupole coupling constants e^2qQ/h are determined from the first-order quadrupole splitting over the temperature range of stability of the mesophases. Within experimental error, (e^2qQ/h) and their temperature dependence are identical for the C_5, C_6 and C_7 carboxylates. At the clearing temperature, the large difference in the ^{23}Na T_1 for the isotropic melt and the mesophase can be interpreted qualitatively by using arguments based on the concept of an anisotropic motion of the Na^+ and $RCOO^-$ ions in the mesophase and an unrestricted motion in the isotropic melt. A qualitative discussion of the observed dependence on the increasing molecular length of the n-alkyl carboxylates is presented for both the ^{23}Na T_1 values and the domain size.

4) The purpose of our recent study (20) was to determine how the properties of the mesophase change with the position of a branching point for a methyl group in the molecule. Sodium 4-methylpentanoate and sodium 3-methylpentanoate were chosen since their molecular length is comparable to that of sodium n-pentanoate. This also extended the data which were available only for two compounds with approximately constant chain length - sodium n-butyrate and sodium isovalerate. Thermotropic ionic liquid crystals sodium 4-methylpentanoate and sodium 3-methylpentanoate have been studied by polarization microscopy and NMR. The quadrupole coupling constant e^2qQ/h of ^{23}Na is obtained for the mesophase and the ^{23}Na spin-lattice relaxation time, T_1, is reported as a function of temperature in both the mesophase and the isotropic melt. A model is presented for the arrangement of the polar groups in the mesophase of all short chain Na carboxylates: the smectic A bilayer consists of $R-COO^-Na^+$ ion pairs with inter-digitated polar groups. The observed dependence of the defect size and e^2qQ/h of ^{23}Na upon the molecular structure is interpreted in terms of this model. A qualitative discussion of possible relaxation mechanisms contributing to the T_1 of ^{23}Na is presented.

5) Deuterium NMR spectra and spin-lattice relaxation times T_1 were obtained (21) as functions of temperature for α-deuterated sodium n-alkanoates ($n_c = 4$-7) in the smectic A and "isotropic" liquid phases. The temperature dependence of the orientational order parameter is found to disagree with the predictions of McMillan's and Woo's theories for the smectic A phase. Reorientational models are presented to explain the experimental order parameters in terms of the structure of the anhydrous solid or the lyotropic gel phase of these compounds. The same models are used in the analysis of reorientational contributions to the ^2D T_1 in the mesophase; order director fluctuations are also estimated to contribute significantly to the relaxation times. The ^2D T_1 temperature dependence in the mesophase resembles that of the ^{23}Na T_1 measured previously, implying shared relaxation mechanisms for the two nuclei. Estimated correlation times for ^2D relaxation in the "isotropic" phase provide evidence for the persistence of local structure characterized by motion on a timescale of tens of picoseconds.

6) It is desirable to compare our measured ^{23}Na quadrupole coupling constants (22) quantitatively with calculations based on actual lateral spacings and long spacings of the sodium carboxylate units. At present spatial parameters are known only for sodium n-butyrate and sodium isovalerate. Therefore, we carried out dilatometric measurements of the molar volumes and X-ray diffraction measurements of the bilayer spacings of all sodium carboxylates for which ^{23}Na quadrupole coupling constants have been obtained. A manuscript is in preparation.

2.3 Viscous Fluids and Glasses

2.31 Introduction

In recent years there has been a significant progress towards a better understanding of the liquid state based on theoretical and experimental work. Particularly, studies in which pressure (1-5) was used as an experimental variable have contributed in a major way to our knowledge of low viscosity ($\eta < 0.01P$) liquids. In our laboratory we have shown that in order to provide a rigorous test of a theoretical model of a fluid or of a specific dynamic process, one has to perform isobaric, isochoric and isothermal experiments. In contrast to work on low viscosity fluids, fewer experimental and theoretical studies dealing with dynamics in viscous fluids ($\eta > 1P$) have appeared. Even from the few high pressure studies of viscous fluids, it has become apparent that extensive systematic experiments which use high pressure as an experimental variable are needed in order to improve our understanding of viscous fluids. One should point out that the ability to vary viscosity over many orders of magnitudes in viscous fluids should provide an advantage over nonviscous fluids in testing the competing theories.

2.32 Viscosity Anomaly in Supercooled Isopropylbenzene

We have carried out extensive measurements of ^1H and ^2D, T_1, $T_{1\rho}$, in selectively deuterated isopropylbenzene (23,24) over a wide range of temperatures and pressures. Isopropylbenzene, which is a simple non-

associative liquid, was chosen for several reasons: i) it supercools readily; ii) its viscosity can be varied over five orders of magnitude over the temperature and pressure range studied; iii) its molecular structure is simple enough to use selective deuteration which then allows a study of ring reorientation and translation separately from the iso-propyl chain reorientation.

Several conclusions regarding the molecular dynamics of supercooled isopropylbenzene were arrived at:

1. The viscosity anomaly at T_K is related to changes in the type of translational rather than rotational motions.

2. Torey's isotropic jump diffusion model can accurately describe the translational motions of isopropylbenzene over a range of viscosities extending to 10^5 poise.

3. The validity of the Debye hydrodynamic equation to supercooled iso-propylbenzene is confirmed over a wide temperature range at isochoric conditions.

4. Volume rather than kinetic (temperature) effects are decisive in determining the extent of the coupling between the rotational and the translational motions.

5. The modified free volume theory developed by Matheson provides an accurate description of the temperature and pressure dependence of the shear viscosity of isopropylbenzene.

6. The dielectric α and β relaxation mechanisms have been detected with NMR experimental techniques.

2.33 Applicability of the Hydrodynamic Equations at the Molecular Level

Considerable attention has been devoted to the relationship between the single particle reorientational correlation time, τ_θ, and the macro-scopic viscosity η of the medium. Our recent study (25) of the deuterium T_1, viscosity and density of several selectively deuterated molecular liquids over a wide range of temperatures and pressures provided impor-tant new information about the validity of the hydrodynamic Debye equa-tion, and about the coupling between the rotational and translational motions in viscous liquids. Since previous studies (26) demonstrated that molecular symmetry rather than permanent dipole moment plays the decisive role in determining the rotational-translational coupling, the main criterium for selecting the compounds for the study was the molecu-lar shape. These compounds were cis-decalin, sec-butylcyclohexane, sec-butylbenzene, n-butylbenzene, isopropylbenzene and toluene. For a more direct comparison, it was desirable to examine the reorientation of the ring segment only, which was achieved by selective deuteration of the ring protons. The reorientational correlation times were obtained from a direct measurement of the deuterium spin lattice relaxation times.

The important conclusions of this study (25) are the following:

1) The Debye equation is successful in providing the link between re-orientational correlation times and shear viscosity in supercooled viscous fluids but only as long as constant density (isochoric) conditions are maintained.

2) Depending on the symmetry (shape) of the molecule the positive or negative deviations from the τ_θ vs. η/T plot are found at high densities.

3) The volume effects and not the kinetic effects (temperature) play the decisive role in determining the degree of the coupling of the rotational and translational motions in viscous fluids.

2.4 Microscopic Understanding of the Sol-Gel Process

2.41 ^{29}Si NMR Study of Sol-Gel Processes Under High Pressure

In our recent studies (27,28) we have investigated the role of pressure on the polymerization kinetics of sol-gel processes. ^{29}Si NMR was previously shown to be a valuable spectroscopic tool for providing a molecular level understanding of the microscopic changes which occur during the sol-to-gel conversion. It was used in our study to monitor the time evolution of all condensed species as a function of pressure in order to explore the possibility of reducing gelation times without affecting the desired characteristics of the resulting wet gels. To the best of our knowledge, this was the first instance of the monitoring of the NMR signal of ^{29}Si nucleus under high pressure to investigate the kinetics of the sol-gel processes.

The time evolution of the $Si(OCH_3)_4$ condensation process subsequent to hydrolysis was monitored as a function of pressure from 1 bar to 5 kbar. It was shown that high pressures have a dramatic accelerating affect on the condensation rate, but do not alter the mechanism via which the polycondensation reaction proceeds. The extent of the condensation rate enhancement was quantitatively evaluated using kinetic principles. Transition state theory was employed to provide a detailed mechanism based on activated volumes for the pressure induced acceleration of the gelation process. In order to ensure that the accelerated kinetics under pressure do not originate from associated pH changes, but rather from volume contraction effects, an experimental comparison was sought between changes produced by pressure and by pH separately. The results confirmed our interpretation.

2.42 Raman Study of the Sol to Gel Transformation Under Normal and High Pressure

Our recent communication (29) studied the reaction kinetics leading to the SiO_2 networks of the wet gels. Although many studies using various techniques such as light scattering, small angle x-ray scattering, NMR, IR and the molybdenum chemical reaction have been undertaken, no investigation of the sol to gel transition using Raman spectroscopy has appeared in spite of the well known suitability of this technique for

studying dried gels and the gel to glass transitions. Importantly, the
Raman spectrum may be measured with no special sample preparation which
could alter its properties and information regarding the gel may easily
be obtained.

The changes in the Raman spectra of the silica sol-gels were exam-
ined as a function of time. The increase of pressure from 1 bar to 3.5
kbar decreased the gelation time from 168 hours down to 6 hours. The
bands associated with the SiO_2 vibrations grow continuously with time
indicating the continuous growth of network particles even after the gel
had been formed.

2.43 NMR, Raman Study of the Effects of Formamide on the Sol-Gel Process

In a collaborative effort with Hench and Orcel (30) we have investi-
gated the effect of formamide on the sol-gel process. Until recently the
production of monolithic samples on a large scale had not been satisfac-
torily demonstrated. A new approach developed at the University of
Florida, using organic drying control additives (DCCA's) such as for-
mamide, greatly facilitates the drying of large monolithic gels. In
order to investigate the role of formamide (NH_2CHO) as a DCCA, high
resolution ^{29}Si NMR, Raman spectroscopy, and N_2 adsorption-desorption
studies have been undertaken to gain additional insights into the charac-
ter of the hydrolysis and the condensation mechanisms, as well as some
structural properties of the resulting silica gel monoliths.

Effects due to formamide (31) have been shown to hinder the hydroly-
sis reaction and favor the condensation of incompletely hydrolyzed spe-
cies, thereby entrapping a larger percentage of alkyl groups in the
silicon polymers of the sol. As a result, larger more highly branched
but less dense silicon networks are formed as confirmed by the Raman
experiments and pore size determinations. Lower drying stresses will be
generated since there are larger pores. Also larger necks will make the
gels stronger and more capable of resisting drying stresses. Therefore,
the net effect of the formamide DCCA is to enhance the rate of drying
without inducing cracks in the gel monolith.

2.44 NMR and Raman Study of the Hydrolysis Reaction in Sol-Gel Process

Before discussing the results of this study, we express our thanks
to Drs. L. L. Hench and G. Orcel for stimulating this study (32).

NMR has frequently been used to study the hydrolysis reaction in
sol-gels. For the first time Raman and NMR were shown in this paper to
provide information on partially hydrolyzed TMOS. The various partially
hydrolyzed TMOS molecules were found to give rise to separate peaks at
different frequencies. The intensities of these peaks evolve in time,
later disappearing as a result of condensation. In both cases, the peak
heights may be related to the concentrations of the species being probed.
The results of the two techniques were found to yield identically the
same results. The hydrolysis rate was found from the initial slopes of
the TMOS decay curve.

Use of the DCCA formamide was found to slow the hydrolysis process. Only a tentative explanation of this phenomena has been proposed. The high viscosity found in the formamide sols will slow the reorientation necessary for the nucleophilic attack to occur. The stronger hydrogen bond formed between formamide and the silicon species will also slow hydrolysis due to steric hindrances.

A combined analysis of the NMR and Raman results led to the conclusion that no OR groups remain in the higher order polymers. Thus, most of the OR groups attached to silicon exist only up to the trimeric species.

High resolution ^{29}Si NMR allowed to distinguish of various species of silicon originating from differing chemical environments. The influence of the substituents on neighboring silicons attached by an oxygen bridge to the probed nucleus was spectroscopically detected and a partial assignment provided.

2.45 Study of Polymerization Processes in Acid and Base Catalyzed Silica Sol-Gels

Raman spectroscopy has been employed in conjunction with ^{29}Si NMR and the molybdenum chemical technique (33) to study the polymerization process of silica sol-gels under pH conditions ranging from 1 to 9.

^{29}Si NMR and the molybdenum chemical method have been simultaneously employed in the determination of the monomer concentration as a function of elapsed time in sols of different pH. The relatively good agreement between the results of the two techniques increased our confidence in the accuracy of the latter, simpler technique.

Several relationships expressing the molybdenum rate constants, κ, in terms of average particle sizes have been developed in the literature for sols polymerizing under acidic conditions (pH < 2). Our study has shown that such functional dependences have limited validity over narrow pH ranges and therefore separate expressions which account for a larger number of parameters must be developed for the respective pH ranges (0 to 2, 3 to 6, 7 to 10).

Most importantly, this study has shown that Raman spectroscopy can be used as a tool to predict and monitor the growth of polymeric particles toward and beyond the gelation point. The relative Raman intensity reflects both the size and the shape of the polymeric structures comprising the wet gel. As a result, fundamental information on particle shape and degree of compactness, which has been recently shown to be of critical importance in particle studies, could be obtained from a detailed analysis of the Raman data. If the growth process proceeds under such conditions of excess hydrolysis water and condensation by nucleophilic substitution, particles of relatively spherical structure result, and the Raman intensity could then be used to provide direct information on particle dimensions.

2.46 Solvent Effects on Condensation Stage of the Sol-Gel Process

Considerable research efforts have recently focused on the use of drying control chemical additives (DCCA) to control pore size distributions and drying stresses incurred in the formation of homogeneous gel monoliths. Formamide has been considered the organic additive of choice in a number of studies devoted to the optimization of the conditions necessary for the production of large scale sol-gel networks composed of uniformly large micropores.

As a result of the great interest in formamide as a drying control chemical additive, we had undertaken a study (34) using ^{29}Si NMR and Raman spectroscopy to gain an improved molecular level understanding of its role on the hydrolysis and condensation mechanisms. The addition of formamide to the silicon alkoxide sols resulted in a drastic reduction in the rate of hydrolysis and led to the formation of extensively branched gel networks of increased porosity and reduced density. An accurate interpretation of these observations generally requires a detailed examination of the chemical and physical modifications which occur upon the inclusion of formamide in the sol-gel matrix. The complexity of the system does not always allow an unequivocal interpretation of the results. In an attempt to provide additional insight into this area, we have undertaken a more systematic study employing a number of other chemically and structurally related organic additives, such as dimethyl formamide, acetonitrile and dioxane. Among the more prominent physical properties which characterize formamide and differentiate it from the conventional solvent, methanol are: high boiling point, high viscosity, large dielectric constant and ability to form strong hydrogen bonds to the system both by donating and accepting electrons. These same properties vary widely in character and magnitude in the other additives selected. These considerations should therefore facilitate predictions regarding the relevance of the various parameters to the gelation process.

The effects of chemical additives on the dynamics of the hydrolysis reaction have been investigated (35) earlier by ^{29}Si NMR. Consequently the present work focuses on the kinetics and mechanism of the condensation process only. Since the use of ^{29}Si NMR has been shown (32) to be limited to the study of the initial stage of the sol-gel process before the emergence of highly condensed oligomeric species, Raman spectroscopy along with the molybdenum reaction technique are currently employed to monitor the progress of the condensation reaction. In addition, scanning and transmission electron microscopy methods have been employed to probe the microstructure of the aggregate particles and thereby confirm the general conclusions derived from the Raman experiment.

By altering the nature and the magnitude of the electrostatic and hydrogen bonding interactions in the sol-gel system, chemical additives were shown to dramatically affect the mechanism of particle aggregation as well as the degree of compactness of the resulting polymeric network.

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