

# Depolymerization Kinetics of Glass-Forming Chalcogenide Melts. Coherence Transfer NMR Studies of Phosphorus Selenide

Robert Maxwell<sup>a</sup>, Hans Erickson<sup>a</sup>, and Hellmut Eckert<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of California, Santa Barbara, CA 93106

<sup>b</sup> Institut für Physikalische Chemie, Westfälische Wilhelms-Universität Münster, Schlossplatz 4/7, D-48149 Münster.

Z. Naturforsch. **50a**, 395–404 (1995); received November 8, 1994

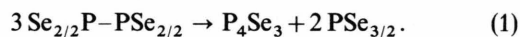
*Dedicated to Professor Müller-Warmuth on the occasion of his 65th birthday*

The kinetics of the depolymerization of a glass-forming phosphorus selenide melt containing 48 at.% phosphorus have been studied using one- and two-dimensional coherence transfer spectroscopic methods. The depolymerization leads to the creation of molecular  $P_4Se_3$ . Two-dimensional spectroscopy indicates that these units are in slow exchange with the residual polymeric matrix, and corresponding rate constants are extracted from temperature dependent one-dimensional coherence transfer experiments. The results are quantitatively consistent with previous temperature-dependent NMR lineshape studies, yielding an activation energy of 109 kJ/mol.

## Introduction

The elucidation of the atomic connectivities that constitute the structure of aperiodic, amorphous, and glassy materials poses a particular challenge to experimentalists and theoreticians alike. Werner Müller-Warmuth was among the first to realize that nuclear magnetic resonance spectroscopy, with its intrinsic focus on the immediate atomic environments, represents an ideal structural tool for such materials. Early on [1] and throughout his career [2] he and his coworkers have led the way in developing powerful quantitative experimental strategies that have helped uncover many fundamental aspects of structure and dynamics in glassy materials. These scientific contributions are of particular value and relevance today in a materials science discipline that is burgeoning with technologically promising but fundamentally poorly understood substances of increasing structural and chemical complexity. A case in point is the large group of glass-forming covalent non-oxidic systems, which has recently come into focus because of their unique optical and electrical properties. Within this group, selenium based chalcogenide glasses are of particular interest due to their infrared transparency and photoconductive behavior [3]. While much of the early work on these systems concentrated on phase diagrams,

macroscopic aspects and bulk thermodynamic properties [4], detailed structural information by means of NMR spectroscopy has become available only during the past decade [5]. In recent years, the quest for a more fundamental understanding of the results obtained has prompted detailed investigations of the molten systems, using in-situ high-temperature NMR spectroscopy [6, 7]. This work has served to characterize the speciation equilibria involved and also provided detailed thermodynamic information [7]. Because of the excellent NMR properties of the  $^{31}P$  isotope, these studies have so far concentrated on phosphorus-selenium melts, which can be regarded as representative model systems for the practically more relevant arsenic-selenium and germanium-selenium glasses. According to the results obtained, the structure of phosphorus-selenium melts differs fundamentally from phosphorus-sulfur melts at comparable compositions and temperatures. While the latter are essentially assemblies of  $P_4S_x$  molecular compounds [8], phosphorus-selenium melts are strongly polymerized. As the temperature is increased significantly above  $T_g$ , however, melts with phosphorus contents  $\geq 40$  at.% P reveal a distinct temperature dependent depolymerization process under formation of molecular  $P_4Se_3$  [6, 7]. In a previous study we have modelled this process in terms of a temperature-dependent speciation equilibrium, in which P–P bonded units disproportionate according to the scheme



Reprint requests to Prof. Dr. H. Eckert.

0932-0784 / 95 / 0400-0395 \$ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72027 Tübingen



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

In the present contribution we show how the kinetics of this process can be quantitatively characterized using high-temperature chemical exchange and coherence transfer  $^{31}\text{P}$  NMR spectroscopy.

## Experimental

A phosphorus-selenium glass containing 48 at.% P was prepared within an evacuated quartz-glass ampoule, heated above  $650^\circ\text{C}$  for 48 hr and quenched rapidly in ice-water. The glass transition temperature ( $T_g$ ) was measured to be  $180^\circ\text{C}$  on a Dupont 912 dual sample differential scanning calorimeter, with a heating rate of 10 K/min. All sample manipulations were carried out in a glovebox under an anhydrous argon atmosphere. Variable temperature NMR spectra were obtained at 121.66 MHz, using a General Electric GN-300 spectrometer equipped with a static probe manufactured by Doty-Scientific. The  $90^\circ$  pulse lengths were measured to be 13  $\mu\text{s}$ . Measurements were conducted in the order of descending temperatures, following thermal equilibration for ca. 30 minutes. Recycle delays were chosen such as to produce representative spectra unaffected by saturation effects.

## Results and Interpretation

Figure 1 shows the previously published  $^{31}\text{P}$  NMR spectra of a glass containing 48 at.% P over the temperature range  $200 \leq T \leq 600^\circ\text{C}$ . At and below the glass transition temperatures, the spectra are dominated by broadening due to wide distributions and large anisotropies of chemical shifts and display resolution no better than previous wide-line or MAS NMR spectra. Above  $225^\circ\text{C}$ , the spectrum reveals a sharpened component at the center and a broad base. As previously discussed [7], the broad base reflects recrystallized  $\text{P}_4\text{Se}_4$ , the formation of which is observed in DSC experiments. With increasing temperature, the broad component decreases in intensity and disappears above  $300^\circ\text{C}$ , presumably due to incongruent melting of  $\text{P}_4\text{Se}_4$ . In this temperature range, the spectrum consists of a dominant peak around 140 ppm, and two minor resonances near  $-70$  and  $70$  ppm, respectively. The latter two peaks are assigned to the basal and apical P atoms of molecular  $\text{P}_4\text{Se}_3$ . The spectral contribution of these resonances increases

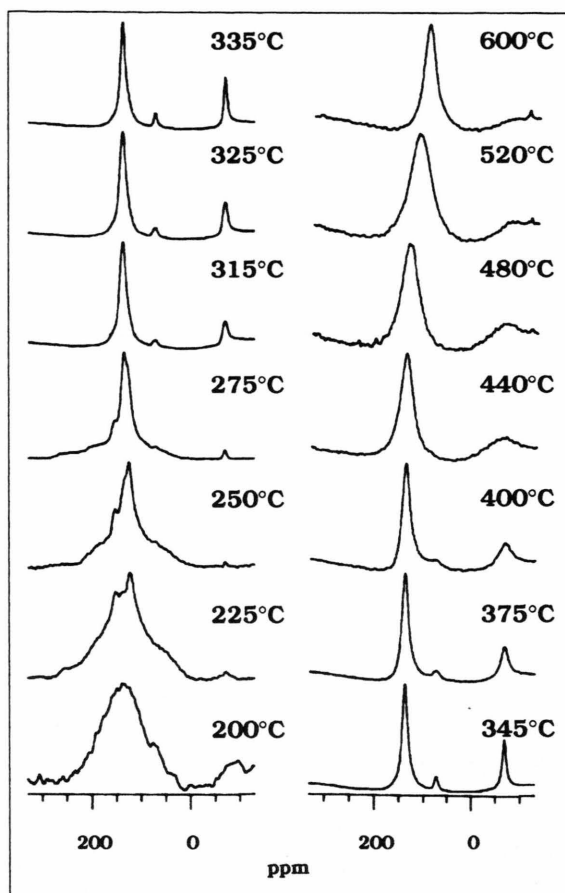


Fig. 1. Variable temperature  $^{31}\text{P}$  NMR spectra of a phosphorus-selenium melt containing 48 at.% phosphorus.

with increasing temperature, reflecting the increasing degree of network depolymerization due to the process schematically described by (1). At temperatures  $T > 375^\circ\text{C}$ , the spectral lineshapes show clear manifestations of chemical exchange, resulting in the eventual coalescence of all three resonances. As previously shown, these spectra can be simulated on the basis of a simplified three-site exchange model, neglecting the intramolecular chemical exchange between the apical and basal P atoms of the  $\text{P}_4\text{Se}_3$  molecules. This rate was assumed to be significantly lower than the rate of interchange between each type of phosphorus atom and the phosphorus atoms of the molten polymeric matrix [6]. The variable-temperature spectra of molten  $\text{P}_4\text{Se}_3$ , shown in Fig. 2, confirm the validity of this assumption. As is evident from this figure, chemical exchange phenomena are slow on this NMR timescale

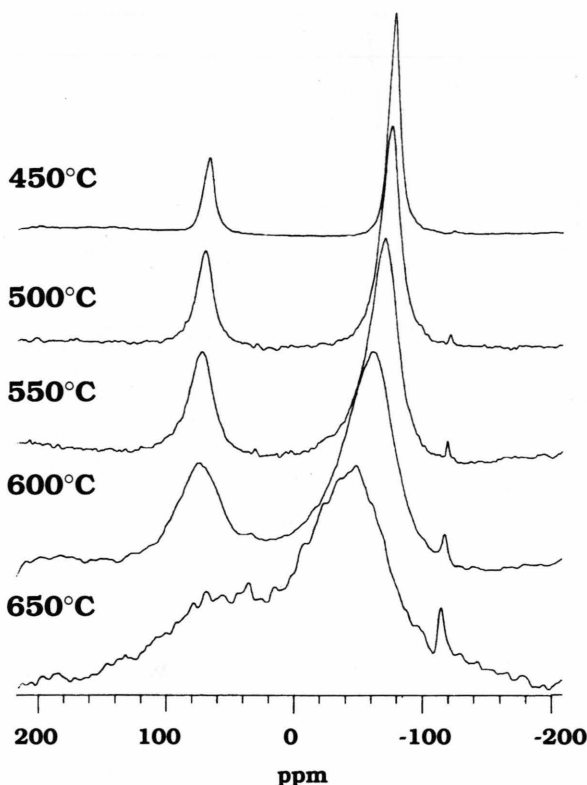


Fig. 2. Variable-temperature  $^{31}\text{P}$  NMR spectra of molten  $\text{P}_4\text{Se}_3$ . Note the absence of chemical exchange phenomena at temperatures below 500°C.

at temperatures below 550°C. Figure 3 reproduces the comparison of experimental and simulated lineshapes as analyzed in detail in reference [6].

The present contribution focuses on the temperature region below 375°C, where all of the chemical exchange rates are too small to affect the  $^{31}\text{P}$  NMR lineshape. In this dynamic regime, it is still possible to probe chemical exchange by one- and two-dimensional pulse techniques. In the two-dimensional exchange spectroscopy experiment [9] shown in Fig. 4, transverse magnetization is first created by a  $90^\circ$  pulse. During the evolution period  $t_1$ , the coherences associated with nuclei in different chemical environments are frequency labeled by their corresponding precession rates in the rotating frame. The second  $90^\circ$  pulse stores these frequency encoded coherences along the magnetic field axis. During the mixing time, chemical exchange or cross-relaxation is allowed to occur, causing a change in the precession frequency for part of the nuclei. Following the mixing time, the third  $90^\circ$

pulse transfers the magnetization back to the transverse plane for the purpose of data acquisition during period  $t_2$ . Subsequent Fourier transformation of the whole dataset with respect to both time domains  $t_1$  and  $t_2$  results in a symmetric stacked or contour plot, in which the occurrence of cross-relaxation or chemical exchange during the mixing time manifests itself in the form of off-diagonal peaks. Figure 5 shows an application of this pulse sequence to the present sample at 330°C, using a mixing time of 15 ms. Both the resonances due to apical and basal P atoms of the  $\text{P}_4\text{Se}_3$  molecules show cross-peaks with the resonance due to the residual polymeric matrix. In contrast, cross-peaks linking the resonances assigned to apical and basal phosphorus atoms in  $\text{P}_4\text{Se}_3$  are noticeably absent, indicating the lack of significant exchange (or cross-relaxation) between both types of P atoms on a 15-ms timescale.

In principle, such two-dimensional NMR experiments can serve to extract coherence transfer rate constants, if the cross-peak intensity is measured as a function of mixing time. For the present system, which is spectroscopically fairly simple, it has great temporal advantages, however, to conduct experiments with similar informational content in a one-dimensional fashion, as illustrated in Figure 6. In this pulse sequence, the equilibrium population difference associated with one resonance is selectively inverted using a DANTE sequence [10]. Relaxation back to equilibrium during the mixing time can now occur via a variety of pathways: zero-quantum dipolar and scalar coupling, spin lattice relaxation and chemical exchange. The final non-selective  $90^\circ$  pulse converts the remaining longitudinal magnetization into observable transverse magnetization. If cross-relaxation or chemical exchange occur, the signal intensities associated with the non-irradiated sites will be affected. Corresponding exchange or cross-relaxation rate constants can then be extracted by systematic measurements under variation of the mixing time. A typical data set is shown in Fig. 7a for the sample at 300°C. Here, the DANTE sequence has been used to selectively invert the magnetization associated with the 140-ppm resonance. As the system re-approaches equilibrium following this perturbation, the intensities of both  $\text{P}_4\text{Se}_3$  resonances at -70 and 70 ppm decrease substantially as the result of coherence transfer via chemical exchange during the mixing period. At longer mixing times, however, the intensities of all three resonances increase again due to the effects of spin-lattice relax-

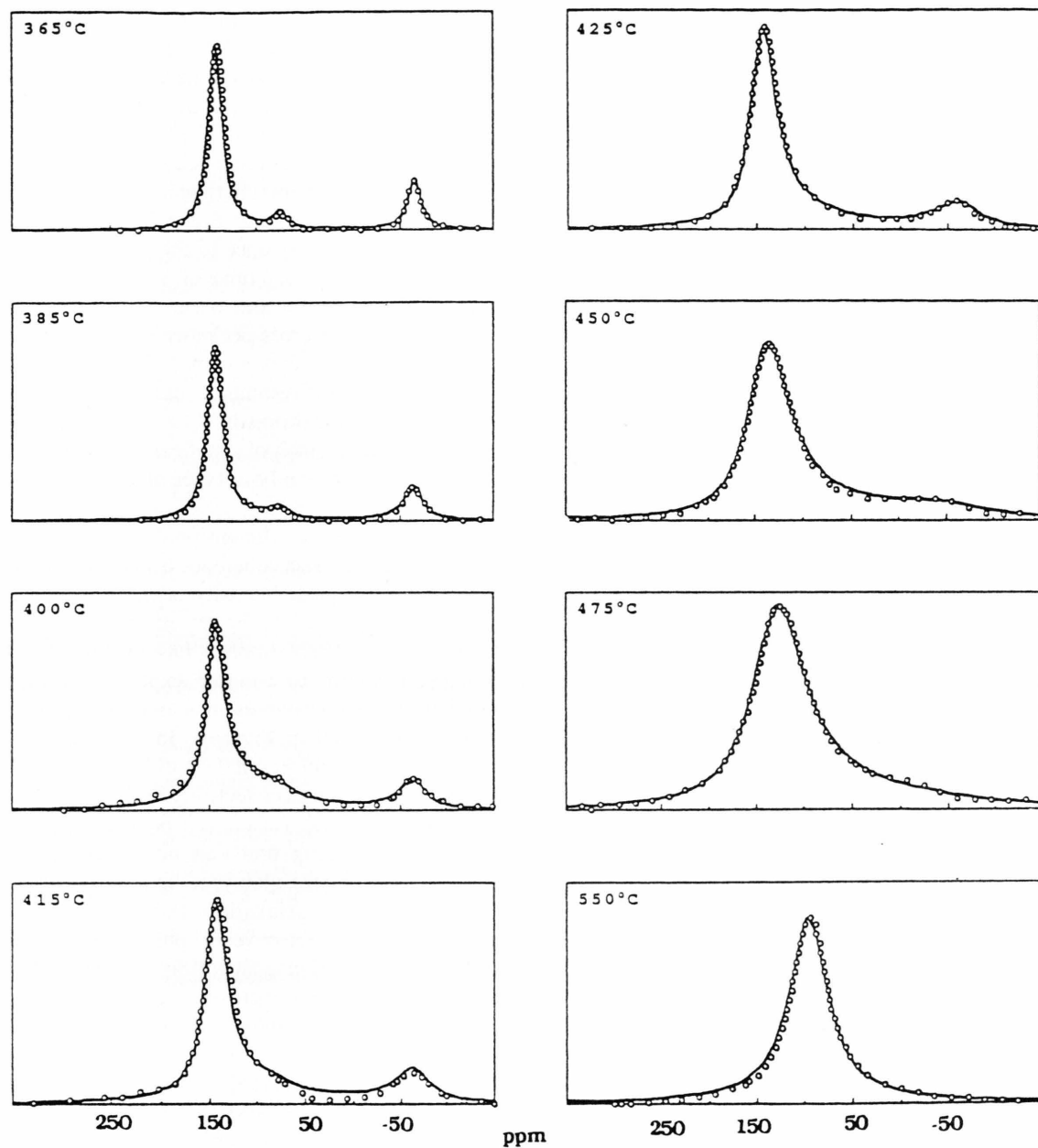
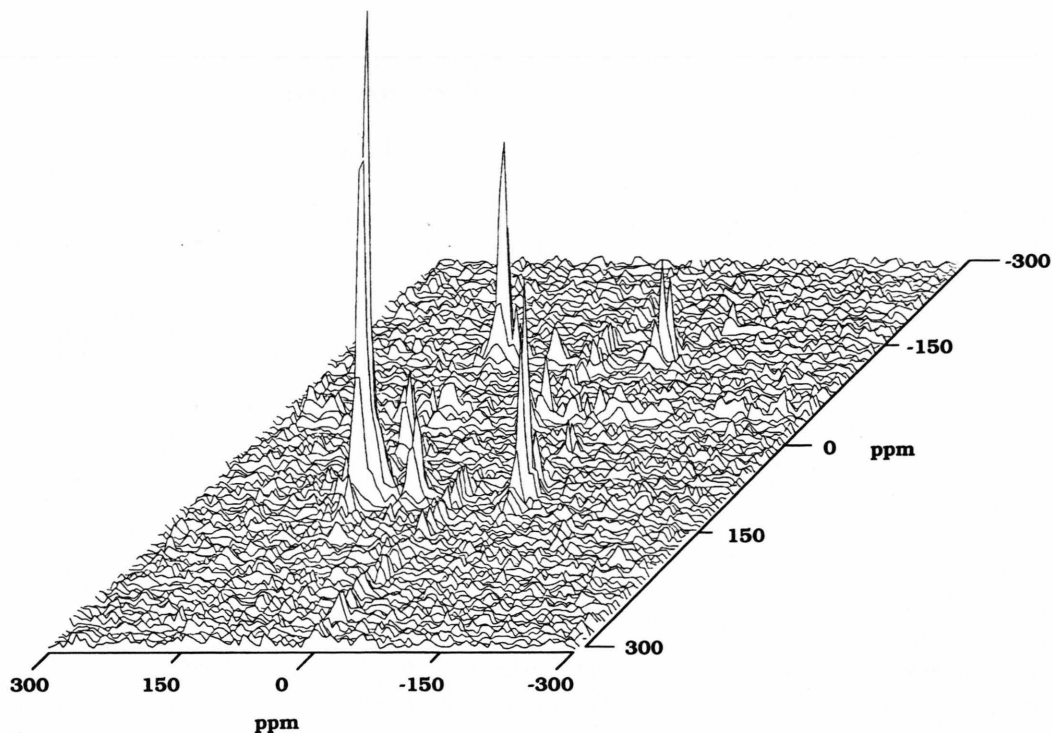


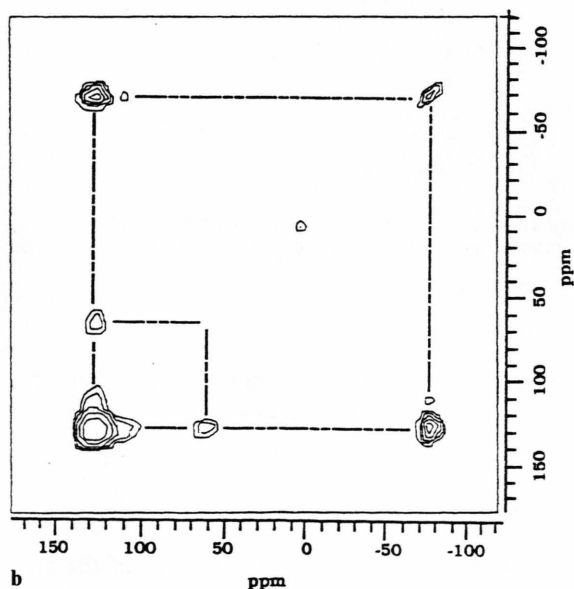
Fig. 3. Experimental (circles) and simulated (solid curves)  $^{31}\text{P}$  NMR spectra of a phosphorus-selenium glass containing 48 at.% phosphorus. The simulations use standard chemical exchange theory as described in [6].



Fig. 4. Pulse sequence used for two-dimensional exchange NMR spectroscopy.



a



b

Fig. 5. Two-dimensional stacked plot (a) and contour plot (b) of a 2-D exchange NMR experiment on a P-Se glass containing 48 at.% phosphorus, at 330 °C. The mixing time used in this experiment was 15 ms.

ation. Figure 7b shows the complementary experiment, in which the peak at  $-70$  ppm, belonging to the basal phosphorus atoms of molecular  $P_4Se_3$  has been inverted by the DANTE sequence. As this perturbed system relaxes toward equilibrium, chemical exchange again causes the intensity of the resonance at 140 ppm to decrease somewhat. The observable effect is smaller in this case, however, because of the smaller overall fraction of inverted spins. It is significant in Fig. 7b, however, that the intensity of the peak at 70 ppm, belonging to the apical P atoms of  $P_4Se_3$  does not change within experimental error over the range of mixing times studied. This result confirms that chemical (and spin-) exchange between the apical and basal



Fig. 6. Pulse sequence used for measuring exchange rates via the one-dimensional saturation transfer method.

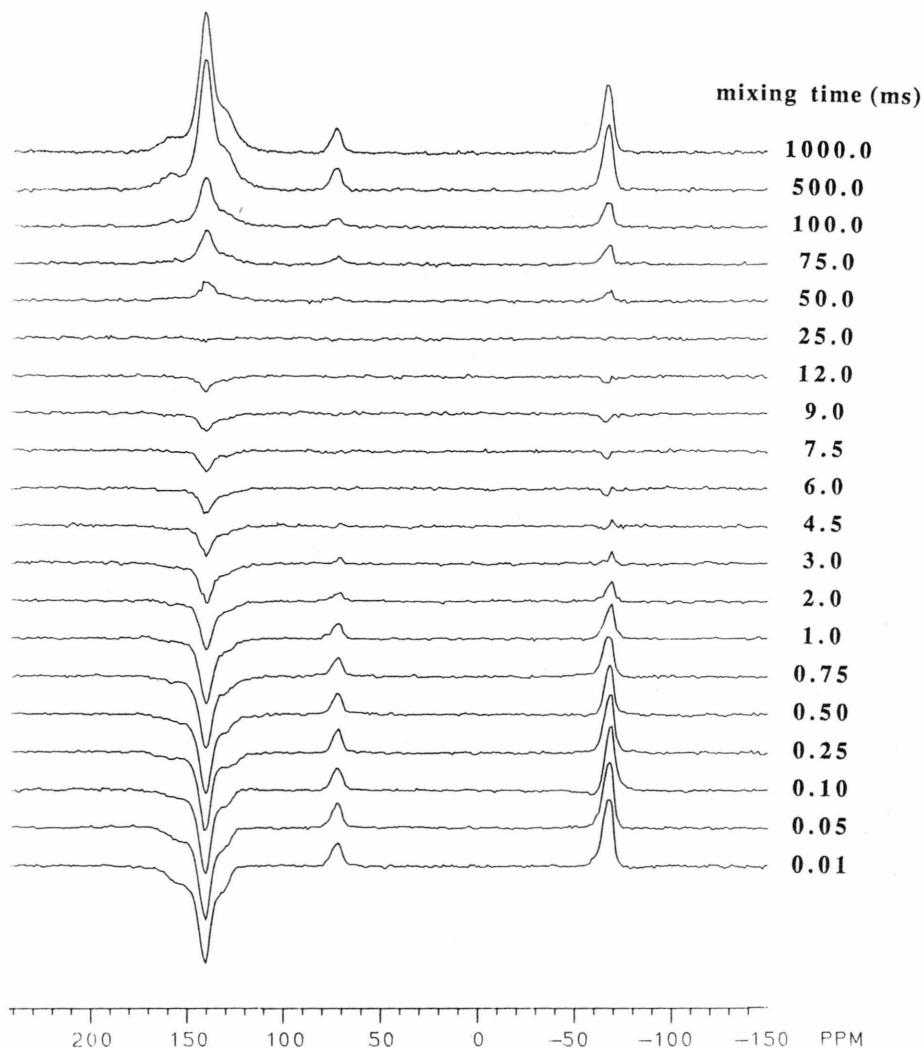


Fig. 7a. Representative data set of a saturation transfer experiment carried out on a phosphorus-selenium glass containing 48 at.% phosphorus, at 300°C. – a) Selective inversion of the resonance at 140 ppm, assigned to P atoms in the polymeric melt.

P atoms of molecular  $\text{P}_4\text{Se}_3$  is substantially slower than exchange involving the polymeric species, thus reinforcing the point made by Figure 2. It is clear, however, that exchange between basal and apical P atoms of  $\text{P}_4\text{Se}_3$  must occur in principle, because the 2-D experiments reveal that both types of P species are in chemical exchange with the P atoms of the polymeric matrix. However, because such interconversion would take at least two steps, a smaller exchange rate is expected for this process than for the interconversion of  $\text{P}_4\text{Se}_3$  and the polymeric melt. The

two-step process is probably not detectable here, because spin-lattice relaxation is too fast.

## Discussion

Figure 8a shows a typical dependence of the normalized intensities for both the inverted resonance at 140 ppm, and of the combined intensities of the  $\text{P}_4\text{Se}_3$  peaks for the data-set shown in Figure 7a. Analogous data have been obtained for seven temperatures

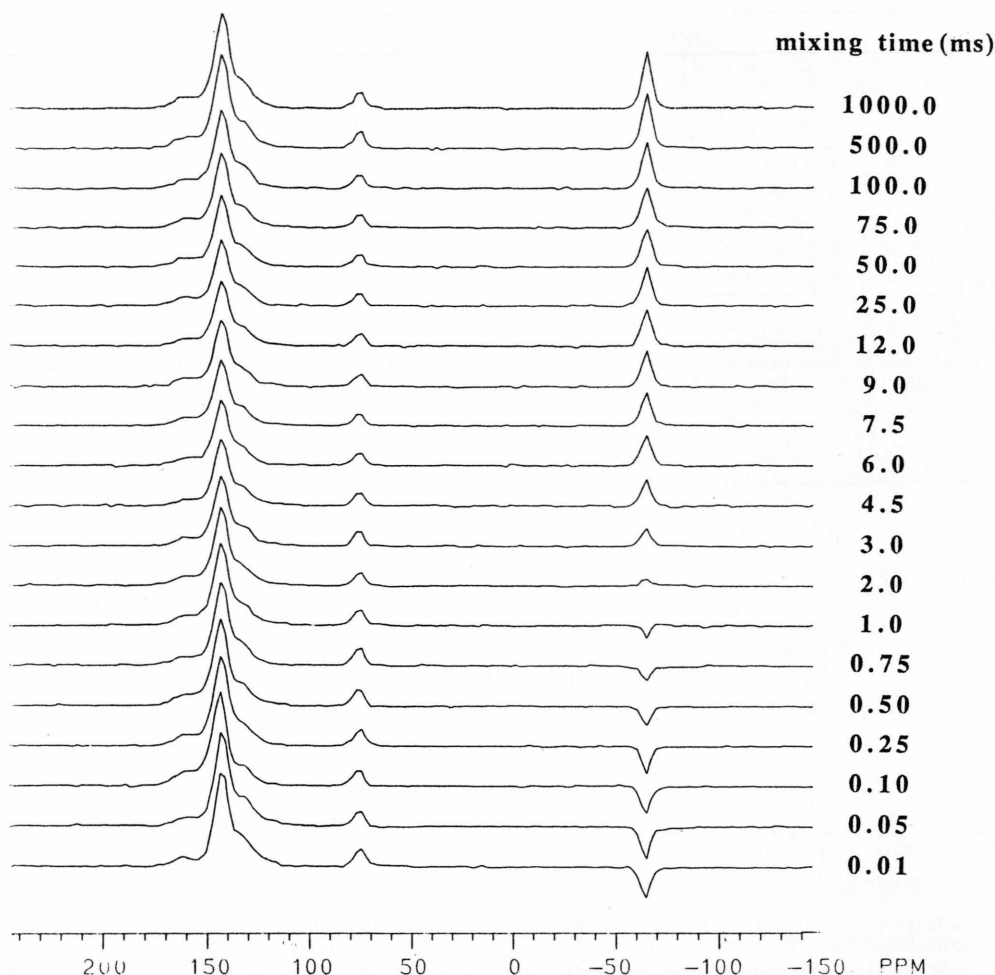


Fig. 7b. Representative data set of a saturation transfer experiment carried out on a phosphorus-selenium glass containing 48 at.% phosphorus, at 300 °C. – b) Selective inversion of the resonance at –75 ppm, assigned to the basal P atoms in molecular  $P_4Se_3$ . Note the absence of chemical exchange between apical and basal P atoms on the timescale of the experiment.

within the range  $280^\circ\text{C} \leq T \leq 345^\circ\text{C}$ . Essentially these curves reflect the combined effect of cross-relaxation via chemical exchange and spin-lattice relaxation. Extracting quantitative rates from these data constitutes solving a kinetics problem [11]. Coupled ordinary differential equations (ODE) with suitable boundary conditions are written describing the system and solved. For a general system, in which scalar coupling is neglected, the form of the equations is

$$\frac{d}{dt}(M_1 - M_1^\infty) = -\left(\sum_{i \neq 1}^n k_{1i} + 1/T_{1,1}\right)(M_1 - M_1^\infty) + \sum_{i \neq 1}^n k_{i1}(M_i - M_i^\infty),$$

$$\begin{aligned} \frac{d}{dt}(M_2 - M_2^\infty) &= -\left(\sum_{i \neq 2}^n k_{2i} + 1/T_{1,2}\right)(M_2 - M_2^\infty) \\ &\quad + \sum_{i \neq 2}^n k_{i2}(M_i - M_i^\infty), \\ \frac{d}{dt}(M_n - M_n^\infty) &= -\left(\sum_{i=1}^{n-1} k_{ni} + 1/T_{1,n}\right)(M_n - M_n^\infty) \\ &\quad + \sum_{i=1}^{n-1} k_{in}(M_i - M_i^\infty) \end{aligned} \quad (2)$$

with the boundary conditions

$$M_i(0) - M_i(\infty) = -B M_i(\infty), \text{ and } B = 1 + F,$$

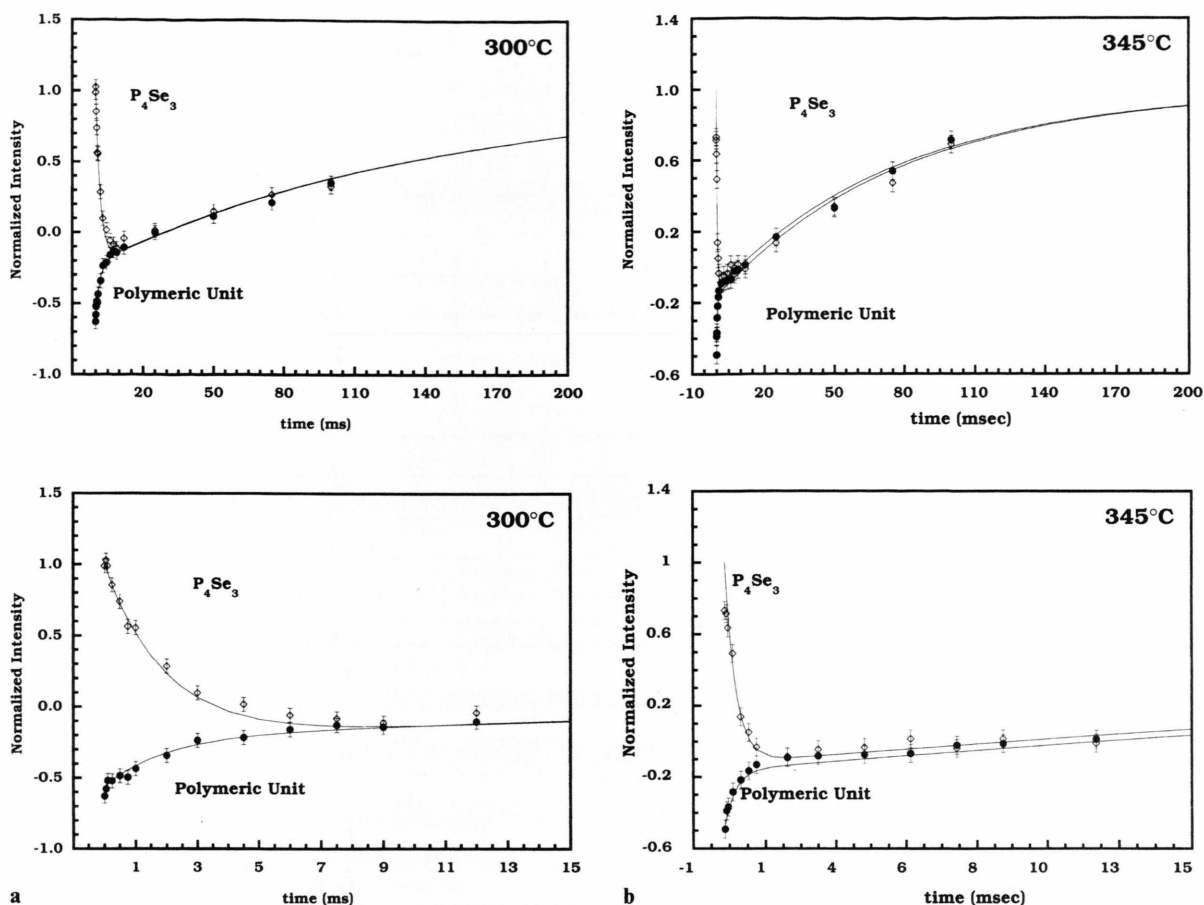


Fig. 8. Representative data set of a saturation transfer experiment carried out on a phosphorus-selenium glass containing 48 at.% phosphorus. Shown are the experimental intensities (normalized to their equilibrium values) of the  $^{31}\text{P}$  resonances as a function of mixing time. Solid curves are theoretical fits to (7), using the parameters listed in Table I. The top part shows the entire data-set, while the bottom part focuses on the short-time behavior dominated by the cross-relaxation effect. — a)  $T = 300^\circ\text{C}$ , corresponding to the data-set shown in Figure 7a. — b)  $T = 345^\circ\text{C}$ .

where  $M_i$  represents whatever spin population is inverted by the DANTE sequence, and  $F$  is the inversion efficiency  $M_i(0)/M_i(\infty)$ .

For all the other resonances the boundary condition  $M(0) - M(\infty) = 0$  holds. The inversion efficiency is determined primarily by instrumental conditions. The number of pulses within the DANTE pulse train, their length, and the interpulse delay all have well-known and calculable effects on the inversion efficiency. Due to instrumental imperfections these parameters must be optimized experimentally prior to data acquisition.

Similarly to the theory of lineshape analysis in the fast exchange limit, the collection of ODE-s can be

written as matrices:

$$d\mathbf{M}/dt = \mathbf{A}\mathbf{M}. \quad (3)$$

The solution of this equation is attained first by diagonalizing  $\mathbf{A}$ :

$$\mathbf{P}^{-1}\mathbf{A}\mathbf{P} = \mathbf{D}. \quad (4)$$

The corresponding matrix  $\mathbf{P}$  can then be used to find the solutions by making the substitutions

$$\mathbf{Y} = \mathbf{P}\mathbf{U} \quad \text{and} \quad d\mathbf{Y}/dt = \mathbf{P}d\mathbf{U}/dt \quad (5)$$

to yield a new diagonal system  $d\mathbf{U}/dt = \mathbf{D}\mathbf{U}$ , which is easily solved for  $\mathbf{U}$  as  $U_i = C_i \exp(-D_{ii}t)$ .

For the present case, a three-spin system at first may seem as the proper basis to approach the problem, however, the system of differential equations is difficult to solve analytically. A more efficient way to approach the solution is to treat magnetization associated with the two resonances of  $P_4Se_3$  as a single spin reservoir. This approach is justified by the fact, evident from Fig. 7b, that on the scale of the mixing time there is no apparent direct spin exchange between apical and basal phosphorus nuclei of the  $P_4Se_3$  molecule. Secondly, Fig. 7a reveals that both types of P atoms exchange with the polymeric matrix with essentially identical rate constants. The latter is indeed expected on the basis of the proposed mechanism. Finally, inversion recovery experiments reveal that the spin-lattice relaxation times of the nuclei in all phosphorus sites are identical within experimental error.

With the above simplifications the problem reduces to that of a two-site exchange matrix of the form

$$A = \begin{bmatrix} -(k + 1/T_1) & Ck \\ k & -(Ck + 1/T_1) \end{bmatrix}, \quad (6)$$

where  $k$  is the corresponding first-order exchange rate constant and  $C$  is the population ratio of the two exchanging sites. The solutions for such a system are known [12] and have been applied to a variety of situations including chemical exchange and spin-diffusion in the solid state [13–15]. In the present application, the solution takes the form

$$\frac{M_{\text{poly}}}{M_{\text{poly}}^{t=\infty}} = 1 - (1 + F) \left\{ \frac{\exp[-(\{1 + C\}k + 1/T_1)t]}{1 + C} + \frac{C \exp[-t/T_1]}{1 + C} \right\},$$

$$\frac{M_{P_4Se_3}}{M_{P_4Se_3}^{t=\infty}} = 1 - \frac{(1 + F) M_{\text{poly}}^{t=\infty}}{M_{P_4Se_3}^{t=\infty}} \left\{ \frac{\exp[-(\{1 + C\}k + 1/T_1)t]}{-(1 + C)} + \frac{\exp[-t/T_1]}{1 + C} \right\}. \quad (7)$$

Experimentally, the best results are obtained, when the resonance at 140 ppm is inverted selectively and coherence transfer to the  $P_4Se_3$  sites is studied as a function of mixing time. Spin-lattice relaxation times were independently measured using an inversion recovery sequence, and the population ratios were determined by careful peak integration. These parameters were used to constrain fits of the experimental data to suitable exchange rate constants  $k$ . These fits are included as solid curves in Figure 8. Table 1 sum-

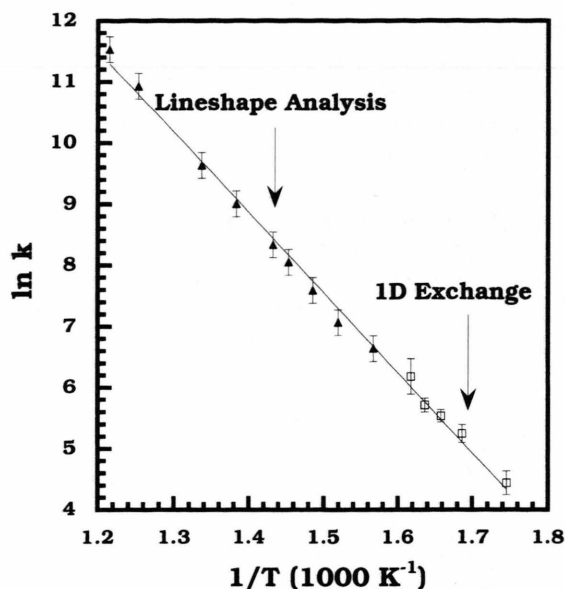


Fig. 9. Arrhenius plot of the chemical exchange rate constants extracted from the saturation transfer experiments (open squares) and comparison with the rate constants extracted from previous simulations of the variable temperature NMR lineshapes at higher temperatures for the same sample [6].

Table 1. Temperature-dependent spin-lattice relaxation times  $T_1$ , chemical exchange rate constants  $k$ , percentage of  $P_4Se_3$ , population ratio  $C$ , and inversion factor  $F$ , in phosphorus-selenium melt containing 48 at.% P. Values listed are fitting parameters, allowed to vary within 10% limits of values actually measured in independent experiments.

$T(^{\circ}\text{C})$	$T_1$ (ms)	% $P_4Se_3$	$C$	$F$	$k$ ( $\text{s}^{-1}$ )
280	143	17.0	0.205	0.44	$78 \pm 10$
300	113	22.4	0.289	0.56	$85 \pm 15$
320	90.9	21.8	0.279	0.55	$191 \pm 26$
330	78.1	22.3	0.287	0.45	$254 \pm 24$
338	63.3	21.3	0.270	0.47	$302 \pm 32$
345	58.8	21.0	0.265	0.47	$583 \pm 148$

marizes all of the parameters used in the present simulations. The Arrhenius plot shown in Fig. 9 compares the data obtained via this method over the temperature range 300–345  $^{\circ}\text{C}$  with those extracted from explicit lineshape simulations at higher temperatures (Fig. 3) [6]. Excellent consistency is observed, suggesting that chemical exchange, not spin-diffusion, is the dominant mechanism of coherence transfer at the lower temperatures. The data from this composite plot yield an activation energy of  $109 \pm 6$  kJ/mol. Assuming linearity to even lower temperatures, we esti-

mate a rate constant of  $0.2 \text{ s}^{-1}$  at the glass transition temperature ( $180^\circ\text{C}$ ). These values may be compared with an activation energy of  $180 \text{ kJ/mol}$  and an exchange rate of  $9 \text{ s}^{-1}$  at the glass transition temperature for  $\text{K}_2\text{Si}_4\text{O}_9$  glass at  $500^\circ\text{C}$  [16]. Furthermore, it is worth mentioning that the behavior observed for phosphorus-selenium glasses differs fundamentally from that observed in amorphous organic chain polymers, where the glass transition is not at all associated with bond breakage, but rather with the onset of long-range mobility averaging intermolecular spatial correlations.

## Conclusions

The results of the present study illustrate the power of in-situ high temperature  $^{31}\text{P}$  NMR for monitoring the depolymerization kinetics in a glass-forming phosphorus-selenium melt. Compared to previously conducted lineshape analyses at high temperatures, the coherence transfer NMR approach used here is particularly useful for providing intimate kinetic informa-

tion at temperatures closer to the glass transition. The rate constant of  $0.2 \text{ s}^{-1}$  obtained via linear extrapolation suggests that the glass transition in chalcogenide systems is characterized by the breakage and formation of covalent bonds, similar to the situation in oxidic glasses. Whether the specific mechanism shown in (1) is responsible for the onset of viscous flow at the glass transitions is a separate question, however. Other bond reorganization mechanisms have been identified in phosphorus-selenium melts [17]. The analysis and separation of these various mechanisms and their respective contributions to the glass transition in these systems is the subject of further study in our laboratory.

## Acknowledgements

This research was supported by NSF grants DMR-8913738 and DMR-9221197 and by a grant from the UCSB Academic Senate. One of us (H.E.) is greatly indebted to Professor Werner Müller-Warmuth for the invaluable scientific training received in his laboratories.

- [1] W. Müller-Warmuth, *Glastechn. Ber.* **38**, 121 (1965); *ibid.* **38**, 405 (1965).
- [2] J. Scheerer, W. Müller-Warmuth, and H. Dutz, *Glastechn. Ber.* **46**, 109 (1973). W. Müller-Warmuth and H. Eckert, *Phys. Rep.* **88**, 91 (1982). M. Grüne and W. Müller-Warmuth, *Ber. Bunsenges. Phys. Chem.* **95**, 1068 (1991).
- [3] P. C. Taylor, *Mater. Res. Soc. Bull.* 1987, p. 36.
- [4] J. Nishii, S. Morimoto, I. Inagawa, R. Iizuka, T. Yamashita, and T. Yamagashi, *J. Noncryst. Solids* **140**, 199 (1992).
- [5] H. Eckert, *Prog. NMR Spectroscopy* **24**, 159 (1992).
- [6] R. Maxwell and H. Eckert, *J. Amer. Chem. Soc.* **115**, 4747 (1993).
- [7] R. Maxwell and H. Eckert, *J. Amer. Chem. Soc.* **116**, 682 (1994).
- [8] T. Bjorholm and H. Jakobsen, *J. Amer. Chem. Soc.* **113**, 27 (1991).
- [9] J. Jeener, B. H. Meier, P. Bachmann, and R. R. Ernst, *J. Chem. Phys.* **71**, 4546 (1979).
- [10] G. Bodenhausen, R. Freeman, and G. A. Morris, *J. Magn. Reson.* **23**, 171 (1976).
- [11] J. Sandstrom, *J. Dynamic NMR Spectroscopy*, Academic Press, New York 1982; J. Kaplan and G. Fraenkel, *NMR of Chemically Exchanging Systems*, Academic Press, New York 1980.
- [12] I. Solomon, *Phys. Rev.* **99**, 559 (1955). A Abragam, *Principles of Nuclear Magnetism*, Oxford University Press (Clarendon), London 1961, p. 335.
- [13] F. Deng, J. Hu, J. Xiong, and Y. Du, *Solid State Nucl. Magn. Reson.* **2**, 97 (1993).
- [14] H. Rumpel and H. H. Limbach, *J. Amer. Chem. Soc.* **111**, 5429 (1989).
- [15] Z. Zhang, J. H. Kennedy, and H. Eckert, *J. Amer. Chem. Soc.* **114**, 5775 (1992).
- [16] I. Farnan and J. F. Stebbins, *J. Amer. Chem. Soc.* **112**, 32 (1990).
- [17] R. Maxwell and H. Eckert, *J. Phys. Chem.* in press