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^{13}C NMR Studies of Poly(propylene oxide) Complexed with Alkali Iodides

by

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^{13}C NMR spectra of poly(propylene oxide) (PPO) and PPO complexed with LiI or NaI, obtained in the solid state using CPMAS techniques, are reported. The methyl carbon exhibits a surprisingly large upfield shift (~2 ppm in PPO_8LiI) due to complexation, which may reflect the negative role played by the methyl group in cation solvation. Line broadening in the complexes is entirely consistent with the increase in the glass transition temperature associated with the formation of the complex. Measurements on PPO_8NaI obtained under a variety of conditions indicate the presence of limited segmental motions on several timescales.

1. INTRODUCTION

Complexes formed between certain polyethers and alkali metal salts have received considerable attention as solid electrolytes for high energy density battery applications (1). Poly(propylene oxide) (PPO) is known to form amorphous and single-phase complexes with a variety of lithium and sodium salts (2).

Previous ^{23}Na nuclear magnetic resonance studies of PPO-NaI samples have demonstrated the presence of enhanced Na^+ mobility in the temperature region just above the glass transition temperature, T_g (3). This observation is consistent with the accumulated experimental and theoretical evidence that the ion transport process is highly dependent on polymer segmental mobility.

Solid-state ^{13}C NMR (4) is a powerful technique for probing polymer chain or segmental dynamics directly and is thus complementary to those methods that focus on the mobile ions. In addition, comparison of the ^{13}C chemical shifts in uncomplexed and complexed PPO offers an opportunity to assess the degree of interaction between the polyether segments and the solvated cations. Natural abundance solid-state ^{13}C spectra utilizing ^{1}H cross polarization and magic-angle spinning (CPMAS) techniques are reported herein for PPO, PPO_8LiI, and PPO_8NaI.

2. EXPERIMENTAL

The host material studied was Parel-58 elastomer (Hercules, Inc.), a sulfur-vulcanizable copolymer of propylene oxide and allyl glycidyl ether. It will be referred to throughout this report as PPO. Preparation of the complexes, in the ratio of eight polymer repeat units per metal cation, is descrbed elsewhere (3).

For NMR experiments, approximately 1 g of solid material was powdered with a cryogenic grinder (Spex Industries) and packed into a 7-mm cylindrical Al_2O_3 rotor. All procedures were carried out in a nitrogen glove bag.

^{13}C NMR spectra were obtained on an IBM Instruments WP-200 spectrometer (operating at a ^{13}C resonance frequency of 50.33 MHz), equipped with a solids accessory consisting of auxillary high-power amplifiers and a magic-angle spinning probe (Doty Scientific).

CPMAS experiments were run at 291, 296, and 330 K, with spinning rates of 1.9 - 3.0 kHz. Decoupling of CH dipolar interactions was achieved with a ^1H decoupling field of 42 kHz. Proton spin-temperature alternation and quadrature phase cycling were used to avoid baseline distortions and other spectral artifacts (5). Recycle delays of 1 s were inserted between acquisitions to permit repolarization of the proton spin reservoir. Direct polarization experiments (DPMAS) were conducted by acquiring the Bloch decay following a single ^{13}C pulse. Other experimental parameters were set as described above for CPMAS experiments.

3. RESULTS AND DISCUSSION

Fig. 1 shows ^{13}C CPMAS spectra obtained for PPO alone and complexed to two alkali salts. Chemical shift assignments listed in Table 1 are made in analogy with solution-state spectral results (6), although the methylene and methine resonance frequencies could well be reversed because of intermolecular packing constraints in the solid state (7). The methyl carbon signal moves upfield upon ionic complexation (see Table 1), to an extent that is roughly twice as great for LiI as compared with NaI. An analogous upfield shift has been reported for sodium tetraphenylborate complexes of poly(ethylene oxide) (PEO) in solution, presumably due to cation binding and a consequent reduction in electron density at the oxygen atom (8). Similar, though smaller, effects have been observed on the polyether carbons of solvent-free siloxane-based polymer electrolytes (9).

Surprisingly, no clearcut chemical shift alterations are found for the CH or CH_2 resonances in PPO. This result may reflect the inferior solvating properties of PPO relative to PEO. In particular the methyl group makes PPO less polar than PEO, as confirmed by dielectric constant determinations (10). Moreover, the steric hindrance of methyl groups exerts a negative influence on the donating ability of the oxygen atoms when the complex is formed (2). The fact that complexation produces upfield shifts for methyl carbons, but no such effect on methine or methylene carbons, also lends credence to this explanation.

The effect of complex formation on ^{13}C spectral linewidths is quite dramatic (see Table 1). In the presence of salts, all peaks are broadened by factors of 4-6, suggesting immobilization of the polymer by Li^+ and, to a slightly smaller extent, by Na^+ (12). This result is consistent with the well-known and much studied increase in T_g upon complex formation (1). From differential scanning calorimetry (DSC) measurements, the central T_g's in PPO, PPO_8NaI, and PPO_8LiI were found to be 213 K, 279 K, and 283 K, respectively (3,11). The fact that the LiI complex yields the largest linewidth reflects the small difference (13 K) between the observation temperature (296 K) and T_g.

Fig. 2 presents NMR spectra of the Na^+ complex obtained under contrasting experimental conditions. Cross polarization (Fig. 2a) and direct polarization (Fig. 2b) give reasonably similar spectral linewidths and relative peak intensities if a delay of 2 s is used between successive acquisitions, demonstrating that ^{13}C spin-lattice relaxation times (T_1's) are quite short (on the order of 1 s) for all the PPO carbons. The efficiency of DP data acquisition thus evidences substantially more PPO motion on the megahertz timescale than that found for corresponding groups in a crystalline solid (4). Even without high-power decoupling, both CPMAS and DPMAS experiments yield well-resolved ^{13}C NMR spectra (not shown). These latter results imply motional averaging of CH dipolar interactions i.e., tumbling at a rate in excess of 50 kHz (13). Similar observations have been reported for the polyether carbons in siloxane-based polymer electrolytes (9).

A rather different spectral appearance results if the CP experiment is conducted without MAS (Fig. 2c). In this case substantial chemical shift anisotropy is observed for the methine/methylene carbon signals: the peak has a breadth of ~30 ppm and a shape characteristic of an axially symmetric shielding tensor. The shift anisotropy for these carbons must exceed ~40 ppm, since noticeable spinning sidebands are observed when MAS experiments are conducted at 2.0 kHz (Figs. 2a and 2b). The rigid-lattice limit for OCH_2 groups, for instance, is 60-80 ppm (14). Both the apparent axial symmetry of the chemical shift tensors, and the short ^{13}C T_1's deduced from DP experiments (above), suggest that these signals are narrowed by molecular motions on the megahertz timescale, though limited angular excursions are indicated by residual broadening and non-Lorentzian lineshapes (15). The methyl carbon resonance has a breadth of only ~3 ppm and an almost-Lorentzian lineshape. This result compares with shift anisotropies of ~30 ppm for typical rigid-lattice cases (16), again suggesting a motional averaging phenomenon. No spinning sidebands are observed for CH_3 peaks in any of the PPO complexes, so the intrinsic shielding anisotropy for these carbons may be unusually small.

Finally, Table 2 presents ^{13}C CPMAS data for the PPO-NaI complex at elevated temperature. No changes in isotropic chemical shift parameters are apparent, but all NMR lines are narrowed appreciably. The latter result demonstrates that the enhanced freedom attained at high temperature provides motional averaging at rates in excess of the decoupling strength (42 kHz) (12). The ^{23}Na linewidth for the mobile cations also undergoes appreciable narrowing in this temperature region, as reported in previous work (3).

4. CONCLUSIONS

^{13}C NMR studies of the solvent-free polymer electrolytes PPO_8NaI and PPO_8LiI show that the methine and methylene carbons in PPO are shifted only slightly (<0.5 ppm), whereas the methyl carbon is shifted upfield by ~1-2 ppm depending on the salt present in the complex. These data suggest that the methyl group interferes with the complexing ability of the polyether segments, and such a result is also consistent with the well-known inferiority of PPO (relative to PEO) as a solvent for alkali salts. Increases in linewidth and immobilization for PPO_8NaI and PPO_8LiI reflect the higher values of T_g that accompany complexation. Nonetheless, limited semental motions on timescales from several kHz to many MHz are inferred from spectra of PPO_8NaI obtained without CP, without high-power decoupling, or without MAS. These motions are observed to be enhanced considerably at elevated temperature (330 K).

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REFERENCES

1. Proceedings of the First International Conference on Polymer Electrolytes, Br. Polym. J. 20(3) 1988.

2a. M. Armand, J.M. Chabagno, and M.J. Duclot, in Fast Ion Transport in Solids, P. Vashishta and G.K. Shenoy, Eds., Amsterdam: North Holland, 1979, p. 131.

2b. M. Vatanabe and N. Ogata, in Polymer Electrolyte Reviews 1, J.R. MacCallum and C.A. Vincent, Eds., Elsevier Applied Science, London, 1987, p.39.

3. M.C. Vintersgill, J.J. Fontanella, S.G. Greenbaum, and K.J. Adamic, Br. Polym. J. 20 (1988) 195.

4a. J. Schaefer and E.O. Stejskal, Top. Carbon-13 NMR Spectrosc. 3 (1979) 283.

4b. Solid State NMR for Chemists, C.A. Fyfe, CFC Press, Guelph, Ontario, 1983.

5. E.O. Stejskal and J. Schaefer, J. Magn. Reson. 18 (1975) 560.

6a. F.C. Schilling and A.E. Tonelli, Macromolecules 19 (1986) 1337.

6b. N. Oguni, S. Shinohara, and K. Lee, Polym. J. (Tokyo) 11 (1979) 755.

7. M.H. Frey and S.J. Opella, J. Chem. Soc., Chem. Commun. (1980) 474.

8. J.A. Ibemesi and J.B. Kinsinger, J. Polym. Sci., Polym. Chem. Ed. 18 (1980) 1123.

9. R. Spindler and D.F. Shriver, J. Am. Chem. Soc. 110 (1988) 3036.

10. M.C. Vintersgill and J.J. Fontanella, in Polymer Electrolyte Reviews, to be published, 1988.

11. J.J. Fontanella, M.C. Vintersgill, M.K. Smith, J. Semancik, and C.G. Andeen, J. Appl. Phys. 60 (1986) 2665.

12. D.L. VanderHart, V.L. Earl, and A.N.Garroway, J. Magn. Reson. 44 (1981) 361.

13. L.V. Jelinski, F.C. Schilling, and F.A. Bovey, Macromolecules 14 (1981) 581.

14a. L.V. Jelinski, Macromolecules 14 (1981) 1341.

14b. Pines, M.G. Gibby, and J.S. Vaugh, Chem. Phys. Lett. 15 (1972) 373.

15. F.A. Bovey and L.V. Jelinski, J. Phys. Chem. 89 (1985) 571.

16a. N. Janes, S. Ganapathy, and E. Oldfield, J. Magn. Reson. 54 (1983) 111.

16b. A. Naito, S. Ganapathy, K. Akasaka, and

C.A. McDowell, J. Chem. Phys. 74 (1981) 3190.
16c. J. van Dongen Torman and W.S. Veeman, J. Chem. Phys. 68 (1978) 3233.
17. A.D. English, J. Magn. Reson. 57 (1984) 491.

Table 1. NMR Parameters for PPO-Ion Complexes

Compound	^{13}C Chemical Shift[a] (ppm)			Linewidth[b] (Hz)		
	CH	CH_2	CH_3	CH	CH_2	CH_3
PPO	75.6	73.6	18.0	45	31	37
	(74.6)[c]					
PPO-NaI	75.9	73.1	17.3	177	212	153
	(74.5)[c]					
PPO-LiI	74.0[d]		16.4	414[d]		199

[a] Referenced to TMS, via *p*-di-*tert*-butylbenzene as a secondary substitution reference. Values for closely-spaced peaks are derived from a curve-fitting routine. Estimated error limits are 0.2 ppm.

[b] Linewidths at half-height, derived from a curve-fitting routine and quoted after subtraction of digital line broadening. The sample temperature is 296 K. Estimated error limits are 10 Hz.

[c] Average of values for CH and CH_2.

[d] Methylene and methine signals are not resolved.

Table 2. Variable - Temperature NMR of a PPO-NaI Complex

Temperature[a] (K)	^{13}C Chemical Shift[b] (ppm)		Linewidth[b] (Hz)	
	CH/CH_2[c]	CH_3	CH/CH_2[c]	CH_3
291	74.2	17.1	371	184
330	74.6	16.9	280	109

[a] From measurements of the exit-gas temperature, corrected approximately as described in Ref. 17.

[b] Obtained as described in Table 1.

[c] Signals are poorly resolved. Chemical shifts are average values; linewidths are composite values from the overlapped peaks.

Figure Captions

Fig. 1. 50.33 MHz ^{13}C NMR spectra of (a) PPO, (b) PPO-NaI, and (c) PPO-LiI. Data were obtained with cross polarization (contact time 500 µs, repetition rate 2 s), magic-angle spinning (2.7 or 3.0 kHz), and dipolar decoupling ($\gamma B_2/2\pi = 42$ kHz). Spectral widths were 20,000 Hz, defined by 4K data points. After accumulation of 1500-2500 transients, the NMR data were processed with a digital line broadening of 20 Hz. The chemical shifts were referenced to tetramethylsilane, via *p*-di-*tert*-butylbenzene as a secondary substitution reference.

Fig. 2. 50.33 MHz ^{13}C NMR spectra of PPO-NaI obtained with various acquisition conditions: (a) CPMAS; (b) DPMAS; (c) CP nonspinning. High-power decoupling ($\gamma B_2/2\pi = 42$ kHz) was employed in each case. A line broadening of 100 Hz was used in processing, and other experimental parameters were as noted in Fig. 1.

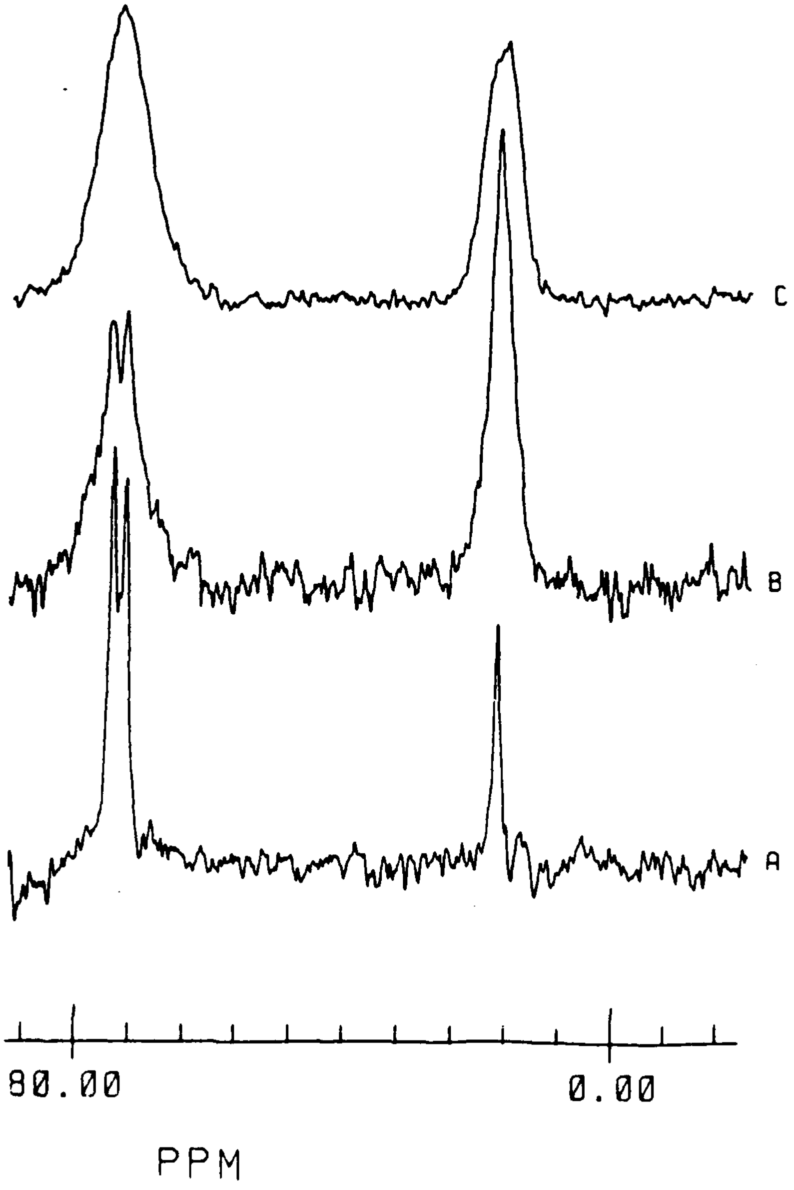

Fig7

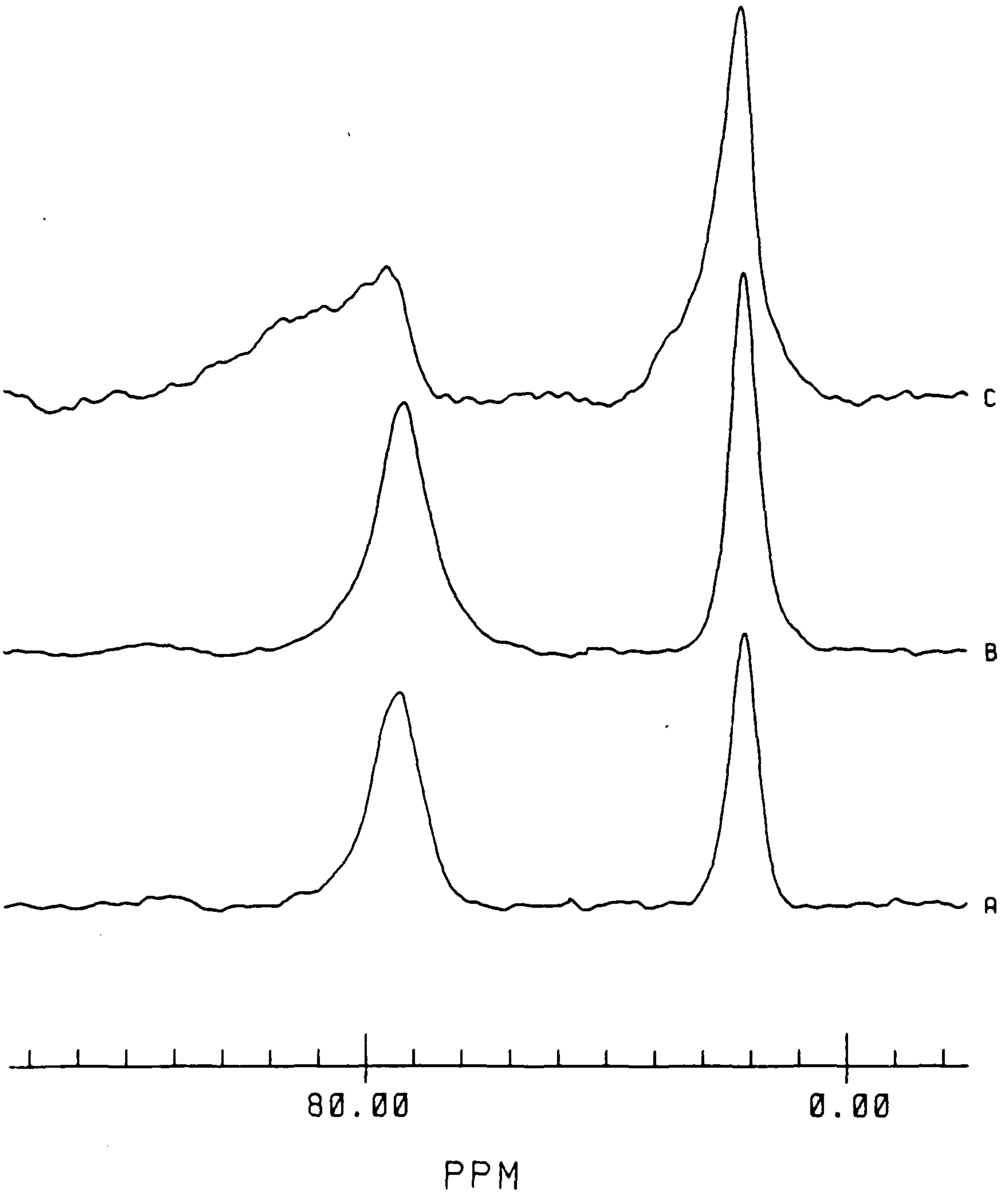

Fig 2