Macromolecules **1982**, *15*, 379–382

bility value about 1.10 ppm at 760 torr and 25 °C compared to the observed value of 2.88 ppm in pure PB is obtained. This result demonstrates vividly the effect of the polystyrene segments in reducing the ability of polybutadiene to accommodate the hydrogen molecules. Extrapolation of Odani et al.'s data[6] for N_2 gas between 40.8 and 100 wt % PS yields a similar result but the effect is much less marked for an extrapolation using their 26.8 and 40.8 wt % data. Nevertheless, it is clear that the polystyrene segments act to diminish the amount of hydrogen dissolved in the polybutadiene fraction of the block copolymers. If an extrapolation to 0% polystyrene is carried out with the hydrogen solubility data at 61.2 and 100 wt % at 0 and 25 °C, values near the solubility in pure PB are obtained, but not for the 50 °C data. If these results are correct, they would suggest that polystyrene in the bulk matrix form is less effective in modifying the PB components than PS in spheres, at least at 0 and 25 °C. As noted in Table II the heat of solution of hydrogen gas in the 61.2% PS sample is almost the same as that in the pure PB.

Thanks to our measurements of the deuterium solubility, we can apply the equation of Frisch and Rogers[7] as modified by Ziegel and Eirich,[8] namely

$$V_f = [18.8/(-\delta\Delta H) + d]^3 \qquad (5)$$

where V_f is the cavity free volume, $\delta\Delta H$ is the difference in the heat of solution in calories per mole of D_2 and H_2 $[\Delta H(D_2) - \Delta H(H_2)]$, and d is the diameter of the H_2 and D_2 molecules, 2.34 Å, to the calculation of V_f for the block copolymers and homopolymers studied in this research. These values are listed in Table II, where an enormous drop is seen between V_f for pure PB and V_f of the block copolymers containing 21.2 and 61.2 wt % polystyrene. V_f rises again in the case of pure PS. These calculations further demonstrate the reduction in the ability of the block copolymers to dissolve hydrogen as compared to the values expected on the basis of a linear additive law.

Finally, one would expect a dual mode of sorption, one mechanism in the pure PB domains and another in the glassy PS domains. All the solubility measurements were made above the glass transition temperature of pure PB, −102 °C for *cis*-1,4-polybutadiene and −48 °C for *trans*-1,4-polybutadiene.[13] The data for pure PB and pure PS show that the solubility in PS is about twice that in PB; however, the solubilities in the block copolymers are not simply the sum of the solubilities in pure PB and PS multiplied by their weight fractions. The PS segments have a marked effect on the PB domains, but the PB segments have little, if any, effect on the solubility of hydrogen in the PS blocks.

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A Study of Polyimide Properties Imparted by the Addition of Lithium Ions

E. Khor and Larry T. Taylor*

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0699. *Received January 19, 1982*

ABSTRACT: Lithium additives have been used as dopants in poly(amic acid) solutions, which, when cured by heating at 300 °C for 1 h, produce thin, flexible, and antistatic polyimide films. Polyimides derived from 3,3′,4,4′-benzophenonetetracarboxylic dianhydride or pyromellitic dianhydride and 4,4′-oxybis[aniline], 3,3′-diaminobenzophenone, or 3,3′-diaminodiphenylcarbinol have been prepared. Thermogravimetric analysis, thermomechanical analysis, X-ray photoelectron spectroscopy, infrared spectroscopy, and elemental analysis have been used to characterize these films. Electrical conductivity has been found to increase significantly with specific polyimides upon lithium chloride addition. The lowered resistivity appears to be a function of increased moisture uptake due to the presence of surface lithium. Other lithium dopants, however, while having surface moisture, do not produce lower resistivity films.

Introduction

In recent years, research into the incorporation of metallic species into electrically neutral polymers has intensified.[1,2] The impetus is primarily directed at the enhancement of electrical, thermal, and mechanical properties of these polymers. The polymer system upon which we are focusing attention is polyimide. In our laboratory, doping with various palladium-containing compounds has been shown to lower electrical resistivity significantly for certain polyimides.[3,4]

The use of lithium dopants in this regard has only been briefly mentioned in the open literature. A polyimide

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Chart I

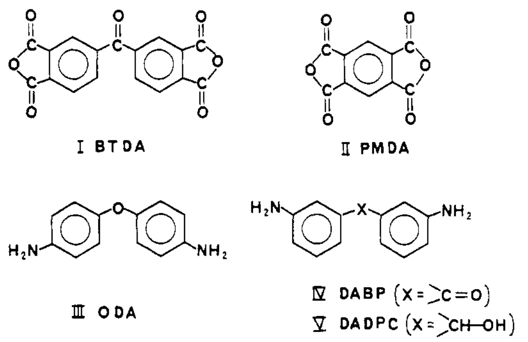

Table I
Thermogravimetric and Thermomechanical Data for Lithium-Containing Polyimides[4]

polyimide constituents	AGT[a]	PDT[b]	% Li
BTDA-ODA	286	540	
BTDA-ODA-Li(AcAc)	317	445	0.30
BTDA-ODA-LiCl	317 (303)[c]	510 (510)	0.17 (0.22)
	326	463	0.51
BTDA-ODA-LiI	321	534	0.17
BTDA-DABP	257	570	
BTDA-DABP-LiCl	253 (257)	510 (500)	0.14 (0.14)
BTDA-DADPC	307	547	
BTDA-DADPC-LiCl	362 (375)	508 (503)	0.22 (0.23)
PMDA-DADPC	340	580	
PMDA-DADPC-LiCl	376	505	0.23
PMDA-ODA	405	580	
PMDA-ODA-LiCl	442 (456)	467 (460)	0.65 (0.54)

[a] Apparent glass transition temperature (°C).
[b] Polymer decomposition temperature (°C). [c] Values in parentheses are for films cured in nitrogen.

doped with 1–10% by weight of lithium chloride or nitrate has been preliminarily reported to exhibit a reduced electrical resistivity.[5] Hygroscopicity has been suggested as contributing to this observation; however, no experimental data were provided. Since lithium was used as counterion with several complexes, the contribution of lithium with regard to reduced resistivity was of particular interest. As a continuation of our efforts in the area of metal ion incorporation into neutral polymers, we wish to report our findings regarding the addition of a variety of lithium dopants to various polyimides for the purpose of altering polymer properties.

Experimental Section

Materials. Monomers were obtained as follows. Pyromellitic dianhydride (PMDA) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) were obtained from commercial sources and purified by sublimation at 215 °C at less than 1 torr; mp 497 and 558 °C, respectively. Oxybis[aniline] (ODA) and 3,3′-diaminobenzophenone (DABP) were obtained from commercial sources and purified by recrystallization. 3,3′-Diaminodiphenylcarbinol (DADPC) was prepared by reduction of DABP. *N*,*N*-Dimethylacetamide (DMAC) was obtained from Burdick and Jackson and used as received. The solvent was reagent grade, distilled in glass, and packed under N_2. All lithium compounds were secured from commercial sources and used after drying in a vacuum oven for ~24 h at 110 °C.

Polymerization. Polymerizations were carried out in solutions containing 20% solids (w/w) by first dissolving the appropriate lithium compound (0.001–0.004 mol) in DMAC under nitrogen. This was immediately followed by dissolving in the same solution the stoichiometric amount of diamine (0.004 mol) and dianhydride (0.004 mol). The resulting solution was stirred at room temperature for approximately 20 h under nitrogen and stored in a refrigerator as its poly(amic acid)–lithium adduct until required for casting.

Preparation and Characterization of Films. Films were prepared and characterized as outlined previously.[4] Depth profiling was performed with a Physical Electronics 550 Auger/ESCA spectrometer. Infrared spectra of thin polymer films were obtained by employing a Nicolet 6000 Fourier transform infrared spectrometer (FT IR).

Results and Discussion

Lithium-doped polyimide films have been prepared for the following dianhydride–diamine pairs: BTDA–ODA, BTDA–DABP, BTDA–DADPC, PMDA–ODA, and PMDA–DADPC (structures I–V, Chart I) The monomer pair PMDA–DABP produced in all cases brittle films which did not meet our requirements. Six candidate lithium compounds were considered for incorporation as follows: the acetylacetonate, chloride, iodide, nitrate, bromide, and hydroxide. The last two were immediately rejected because both were found to be insufficiently soluble in the solvent system employed.

Good-quality films were obtained for the remainder of the soluble compounds except for lithium nitrate, which always yielded very brittle films, probably due to thermal oxidative degradation. Since the best conductivity results were obtained with lithium chloride, it served as the primary dopant. Most films were smooth, yellow to dark brown, and, in most instances, flexible. The normal lithium content in most of our films (Table I) was found to be about half its theoretical value, suggesting that a significant quantity is lost during thermal (300 °C) imidization.

Thermogravimetric and thermomechanical data for the films are listed in Table I. In most instances, thermal stability (polymer decomposition temperature (PDT)) decreases, the extent depending on the amount of dopant present. The apparent glass transition temperature (AGT), on the other hand, increases but is less affected by dopant concentration. This leads to the tentative conclusion that the additives influence regularity of structure, explaining the higher apparent glass transition temperature.[6] Similar trends in thermal properties were produced when films were cured in nitrogen rather than air.

No appreciable lowering of volume or surface resistivities was observed except when the dopant was lithium chloride and the monomer pair was either BTDA–ODA or PMDA–ODA (Table II). With the former LiCl-doped monomer pair, the typical volume resistivity range was 10^6–10^{10} Ω-cm as compared to undoped films with values greater than 10^{18} Ω-cm. These data, however, were obtained for films measured after air-drying. Upon subsequent vacuum drying at 110 °C for 12 h, volume resistivities were found to increase to 10^{12}–10^{14} Ω-cm. Finally, when resistivity measurements were carried out in a drybox after heat vacuum drying, values in the vicinity of 10^{16} Ω-cm were observed. The surface resistivities, likewise, followed the same trend. This suggests that the primary improvement in conduction is due to the ability of the lithium ion to pick up moisture although no noticeable droplet formation was observed on the surface.

For the monomer pair PMDA–ODA lowering of volume resistivity was only observed when dopant concentration was relatively high. For a film cured in air having 0.65% lithium, the volume resistivity was found to be 1.64×10^{10} Ω-cm. The volume resistivity, however, increased to 7.2×10^{15} Ω-cm on vacuum drying. A film cured in nitrogen containing 0.54% lithium, on the other hand, gave volume resistivities of 4.4×10^6 and 1.9×10^{12} Ω-cm upon air-drying and vacuum drying, respectively. A possible ex-

Table II
Resistivity and XPS Data of Lithium-Containing Polyimide Films

monomer pair	dopant	% Li	volume resistivity, Ω-cm	surface resistivity, Ω	film side	BE, eV	electron counts Li(atm)/ Li(glass)
BTDA-ODA	Li(AcAc)	0.30	5×10^{16}	$>10^{16}$	atm	50.75	1.05
					glass	51.00	
BTDA-ODA	LiI	0.17	7×10^{15}	$>10^{16}$	atm	50.6	1.25
					glass	50.3	
BTDA-ODA	LiCl	0.51	4×10^{6}	4×10^{4}	atm	54.2, 50.65	1.17, 0.88
				3×10^{6}	glass	54.75, 50.46	
PMDA-ODA	LiCl	0.54	4×10^{6}	1.1×10^{9}	atm	50.9	1.06
				3.6×10^{4}	glass	50.8	
BTDA-DADPC	LiCl	0.23	1×10^{15}	$>10^{16}$	atm	50.3	0.99
					glass	50.6	
PMDA-DADPC	LiCl	0.23	4×10^{15}	$>10^{16}$			
BTDA-DABP	LiCl	0.14	1×10^{15}	$>10^{16}$			

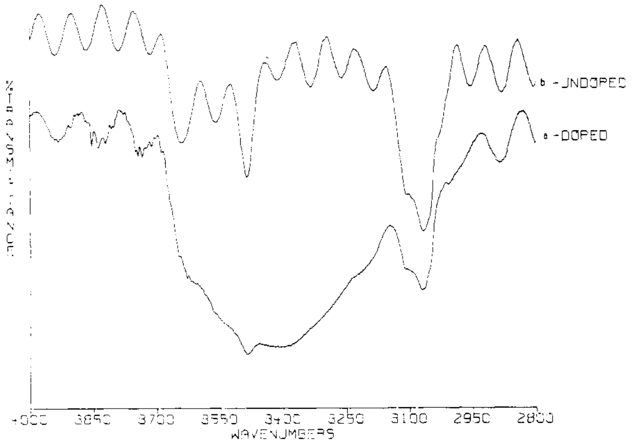

Figure 1. IR spectrum of BTDA–ODA (a) doped and (b) undoped films.

planation for this observation lies in the brittleness of the air-cured film vs. the more flexible nitrogen-cured film. A more homogeneous distribution of lithium might then be expected in the nitrogen-cured film, which may facilitate better electrical conduction.

The presence of water in the BTDA–ODA–LiCl film was verified by Fourier transform infrared spectroscopy (FT IR). Figure 1a illustrates the hydrogen–oxygen stretching vibrational region for the above film. The strong IR absorption suggests the presence of a relatively large quantity of water when contrasted to its undoped counterpart, which shows very little evidence for moisture (Figure 1b). On extending this examination, we observed a comparable amount of water in all doped films regardless of their resistivity. This implies a further factor is necessary for reduced resistivity, perhaps the distribution of lithium throughout the film, although scanning electron microscopic study of both types of films to date reveals no major surface differences, where, typically, only a smooth surface was obtained.

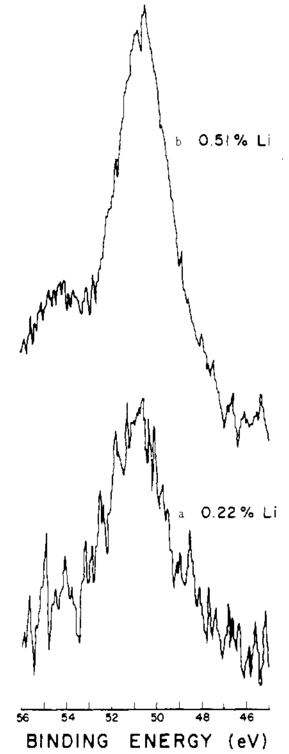

Figure 2. Concentration dependence of lithium 1s photopeak.

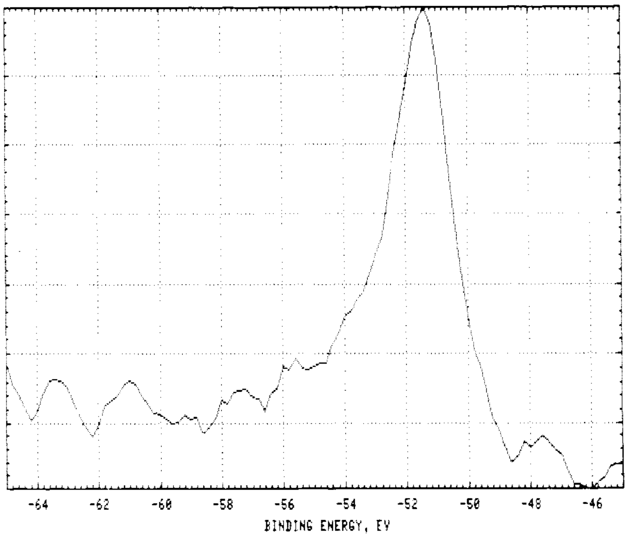

Figure 3. Li(I) XPS region before depth profiling of BTDA–ODA–LiCl film.

X-ray photoelectron spectroscopy (XPS) has proven useful in the study of lithium speciation in these polymers. Figure 2a shows a typical spectrum obtained for the lithium 1s photopeak. The primary lithium peak for all doped polyimides was found to be around 50.5 eV regardless of the measured resistivity. At higher dopant concentrations, a secondary peak, not always observed and much less intense, appears around 55.0 eV (Figure 2b). According to Povey and Sherwood,[7] the peak at 50.5 eV is characteristic of lithium in Li_2O, while the peak at 55.0 eV is more characteristic of lithium in LiCl. We find no evidence that spectrometer conditions can give rise to photochemical decomposition leading to lithium oxide as suggested by Povey and Sherwood. A film irradiated by X-rays after 30 min gave the same spectrum as that of the same film irradiated after 2 h. This would be unexpected if photo-

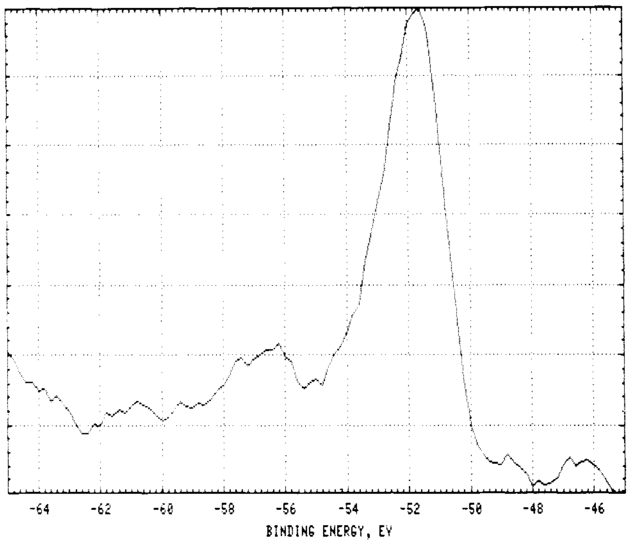

Figure 4. Li(I) XPS region after depth profiling of BTDA-ODA-LiCl film after 30 min.

decomposition were occurring during X-ray photoelectron spectroscopic examination. It is reasonable, therefore, to conclude that lithium oxide may be generated during thermal imidization via Li^+ reaction with the released water, followed by hydrolysis and dehydration. Similar lithium XPS observations have been made on films doped with Li_2PdCl_4. The peak at ~55.0 eV, which appears only at high lithium concentrations, arises when, no doubt, insufficient water of imidization is released to solvate all the lithium ion.

The nature of lithium on the film surface compared to the bulk is of interest. In other words, is the "lithium oxide-like" material dispersed throughout the film rather than on the film surface? First of all, the atmosphere side and glass side of each film show a comparable number of electron counts for lithium (Table II). This observation is contrary to our palladium findings in that the atmosphere side of the film contains appreciably more palladium than the glass side of the film. Information regarding the lithium content and chemical state inside the lithium-doped film has been obtained from angular and depth profile studies. At a 90° X-ray incidence angle, the spectrum of highly doped BTDA-ODA-LiCl is as per Figure 2b. On shifting to an incidence angle of 11°, the secondary peak is diminished significantly relative to the main peak. This suggests that "LiCl" is found only in the matrix of the polymer, whereas, "Li_2O" occupies the surface as well as the bulk. On depth profiling normally doped BTDA-ODA-LiCl for 30 min (argon ion sputtering), the shoulder at 55.0 eV, which originally could not be discerned, has grown to a distinct peak (Figures 3 and 4). The ratio of "LiCl" to "Li_2O" through the film appears to be a constant since spectra after 60- and 90-min sputtering are similar. One concludes, therefore, that "LiCl" is present in small quantities and that most has been converted into "Li_2O" during thermal imidization.

The primary question left unanswered is that of why some films conduct and others do not, when they apparently are identical in all aspects except monomer pair combinations. That there is some electrical conduction is realized due to the differences of volume resistivities measured. The final answer probably lies in an understanding of the mode of conduction in these lithium-doped films. It is reasonable to conclude that the quantity of Li(I) and consequently, its manner of distribution in the bulk of the polyimide films play pivotal roles in addressing this question.

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Polyelectrolyte Properties of Sodium Hyaluronate. 1. Salt Exclusion in Sodium Chloride Solution

Robert L. Cleland

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755.
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ABSTRACT: Experimental data from dialysis equilibrium on exclusion of NaCl from solutions of sodium hyaluronate are examined in terms of the Poisson-Boltzmann treatment of the uniformly charged rigid-rod model for polyions in excess salt. Values of the exclusion coefficient are fitted reasonably well by this model, although uncertainty in the data permits an estimate of the rod radius a only in the approximate range a = 3.5 Å (from the polymer molal volume) to a = 7.5 Å (from the estimated distance of closest approach of polyion and counterion).

The interpretation of data from the potentiometric titration of solutions of hyaluronic acid in the following paper[1] involved a consideration of polyion-small-ion interactions in polyelectrolyte solutions. The study of this problem led to a reexamination of existing data from dialysis equilibrium on salt exclusion[2-4] in solutions of sodium hyaluronate with NaCl. In this work the consequences of the treatment of salt exclusion by the Pois-